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APRIL 9 - 12, 2000
PORTO, PORTUGAL

**PROCEEDINGS OF THE
2000 SUGAR PROCESSING
RESEARCH CONFERENCE**

**APRIL 9-12, 2000
PORTO, PORTUGAL**

**Sponsored by
Sugar Processing Research Institute, Inc.
New Orleans, Louisiana**

December 2000

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PREFACE

The 2000 Sugar Processing Research Conference is one in a series of Conferences held in alternate years to provide a forum for the exchange of information among technical leaders of the sugar industry and to report on new and noteworthy developments. The Conference is sponsored by Sugar Processing Research Institute, Inc., (S.P.R.I.).

The program for this Conference was arranged by Dr. Chung Chi Chou and Mary An Godshall. The Conference Coordinator was Shirley T. Saucier, assisted by Xavier M. Miranda. These Proceedings were edited by Mary An Godshall.

Sugar Processing Research Institute, Inc., acknowledges the contribution in kind to the support of this conference by the Southern Regional Research Center, Agriculture Research Service, United States Department of Agriculture. Also acknowledged is the support of RAR - Refinarias de Açúcar Reunidas, and its staff, in contributing to the support and success of this Conference.

The series, Proceedings of the Sugar Processing Research Conference, of which this is the tenth issue, continues the Proceedings of the Technical Sessions on Cane Sugar Refining Research, which was published every other year from 1964 to 1980. For individual copies of this volume as well as back issues of the former series as long as the supply lasts, write to Sugar Processing Research Institute, Inc., 1100 Robert E. Lee Blvd., New Orleans, Louisiana 70124. Before 1986, Proceedings were published by the Agriculture Research Service, U.S. Department of Agriculture. Since 1988, Proceedings have been published by the Sugar Processing Research Institute, Inc.

Mary An Godshall
Managing Director
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SUGAR PROCESSING RESEARCH INSTITUTE, INC.

Sugar Processing Research Institute, Inc., is an independent non-profit research institute supported by the international sugarcane and sugarbeet production and refinery industries and their supplier and user companies. The Institute is housed at the Southern Regional Research Center of the United States Department of Agriculture, Agricultural Research Service, under a Memorandum of Understanding with U.S.D.A. The association with U.S.D.A. offers many synergies for the benefit of the sugar industry. The S.P.R.I. organization is unique in that it undertakes both beet and cane sugar processing research.

The history of the Institute began in 1939 with formation of the Bone Char Research Project at the National Bureau of Standards in Washington, D.C., under the direction of Dr. Victor Dietz. In 1963, it moved to New Orleans, Louisiana, and became the Cane Sugar Refining Research Project with Dr. Frank Carpenter as its director. In 1981, under Dr. Margaret Clarke, its scope was greatly expanded when it became Sugar Processing Research, Inc. In 1991 it was renamed Sugar Processing Research Institute, Inc. After the untimely death of Margaret Clarke in 1998, the Institute was led for a brief period by Dr. Chung Chi Chou and is currently under the leadership of Mary An Godshall.

S.P.R.I. seeks to devote its best efforts to be a center of excellence in sugar technology research for the sugar industry and the member companies of S.P.R.I.

FORWARD

The theme for this Millennial year conference was, “What do we need to do for the Twenty-First Century in Sugar Processing?” These Proceedings cover a diverse set of topics, reflecting the wide ranging activities and interests of the sugar industry.

Prof. Mathlouthi provides a look back at what was accomplished in the Twentieth Century, and then takes a look to the future. Prof. Thibault, this year’s S.P.R.I. Science Award Winner, explores innovative uses of beet pulp, to add value to the crop. In discussion of a topic that is sure to be a major theme in the Twenty-First Century, Dr. Robin Rogers describes the concepts of Green Chemistry and what a carbohydrate-based economy might look like. He points out that the sugar industry has taken many steps in the right direction with pollution abatement, co-generation, and other initiatives. Tom Schwartz discusses biotechnology in the beet sugar industry, another area that can only expand in the future.

Other papers discuss innovations, such as electrodialysis as a purification technique, use of nuclear magnetic resonance to study sucrose solubility, bioremediation of resin effluents, the continued expansion of near infrared technology in the cane and beet industry, and advances in membrane technology, to name but a few. Several papers discuss color and degradation of invert to produce color and lead to sucrose loss, perennially important subjects for the industry. The effect of harvest systems on cane juice quality are examined in depth by two papers. Dextranase use is usually associated with cane sugar operations, but a paper herein discusses its successful use in a beet factory during a particularly challenging harvest period.

For the first time, these Proceedings also feature a Special Review Section. The topic of molasses exhaustion is reviewed in detail by Professor Martine Decloux, who undertook Sabbatical studies at S.P.R.I. during 2000.

It is hoped that the reader of these Proceedings will find much interesting material and food for thought within its pages.

Mary An Godshall
November 2000

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2000 S.P.R.I. Science Award

JEAN-FRANÇOIS THIBAUT



The S.P.R.I Science Award is offered biennially to an outstanding scientist whose research and development accomplishments have been distinguished by their originality and by their contribution to the sugar processing and production industry. The 2000 S.P.R.I. Science was presented to Professor Jean-François Thibault.

Jean-François Thibault was born on November 4, 1950, in France. He received his graduate Engineer degree from ENSIA in 1973 and the Doctorate of Sciences (*cum laude*) from the University of Nantes in 1983.

He is a Research Director at the Institut National de la Recherche Agronomique (INRA) in Nantes, France, where he heads the Cell Wall Polysaccharide Group, and is also currently the President of the INRA

Nantes Research Center, a renowned research center with 100 scientists and 100 technicians.

Dr. Thibault has promoted research into adding value to sugarbeet pulp, an abundant by-product of sugarbeet processing in Europe. Using his scientific background in polysaccharides, he has separated the sugarbeet pulp into various interesting fractions, leading to the finding that ferulic acid is a structural feature of sugarbeet pectins, a fact that can be utilized to produce a high-gelling pectin from sugarbeet pulp. His research in value-added products from sugarbeet pulp has included the production of dietary fiber, a natural ion-exchanger for pollution abatement of heavy metals, production of natural vanillin, cellulosic biodegradable films for food and non-food applications, and cellobiose.

Dr. Thibault has authored more than 150 original peer-reviewed papers, has given more than 180 presentations at congresses and symposia, and more than 30 invited lectures. He holds 7 patents.

On the personal side, Dr. Thibault is married and has three children.

2000 S.P.R.I. Industrial Technology Award

LUIS ROCHA SAN MIGUEL BENTO



The S.P.R.I. Industrial Technology Award is given for the purpose of promoting technology in sugar processing and production. It is to be offered biennially to one outstanding individual whose contribution to the industry in the development of technology, or implementation of technology, has been distinguished by its originality and the resulting benefit to the industry.

Luis Rocha San Miguel Bento was born in Cantanhede, Portugal, on November 22, 1940. After his grammar school, Luis entered Coimbra University in 1958 where he completed his B.Sc. in Chemical Science, the first part of a six-year course of Chemical Engineering, finishing in 1964 in Faculdade de Engenharia of Oporto University.

Luis started to work at RAR in 1965 as assistant to the Production Manager. In 1970 he became Process Manager. In 1978 he attended the first Cane Sugar Refiners Short Course at Nicholls State University in Thibodaux, Louisiana.

His research interest in the sugar industry started with the application of ion exchange resins and salt effluent treatment. He studied sugar colorants, their identification and their behavior during cane sugar refining. His work has been presented and published in about 30 technical papers and patents. As a result of these accomplishments, Luis received the SIT Crystal Award in 1995, the SIT George and Eleanore Meade Award in 1989 and 1993, and a Gold and a Silver Medal at the IENA Exhibition, Nuremberg, Germany, in 1989 and 1990. Luis is a Director of SPRI and a member of the Research Advisory Committee of SPRI. He was President of SIT in 1998/99, and is a member of CITS, ISSCT, AVH and IBET. Luis also is a member of the Portuguese Academy of Engineers, of IFT and AAAS, and is the representative of Portugal to ICUMSA.

Luis lives in Matosinhos, Portugal, and is married to Alexandrina Maria, affectionately known as Dina. Luis and Dina have two daughters, Inês, 24, a Chemical Engineer, and Rita, 20, a student of Marine Biology in Azores University.

Winners of the S.P.R.I. Awards

Winners of the S.P.R.I. Science Award and Their Lectures

- 1986 Andrew Van Hook, Chemistry Department, Holly Cross College, Worcester, Massachusetts
Events in Sugar Crystallization
- 1988 Leslie Hough, King's College London, Department of Chemistry, Kensington, London
Sucrose, Sweetness and Sucralose
- 1990 Giorgio Mantovani, University of Ferrara, Italy
Growth and Morphology of the Sucrose Crystal
- 1992 Riaz Kahn, Poly-Bios, Trieste, Italy
Chemical and Enzymic Transformations of Sucrose
- 1994 Frieder W. Lichtenthaler, Institute of Organic Chemistry, Technical University of Darmstadt, Germany
Computer Simulation of Chemical and Biological Properties of Sucrose, the Cyclodextrins and Amylose
- 1996 Pascal A. Christodoulou, Hellenic Sugar Industry, Thessaloniki, Greece
Energy Economy Optimization in the Separation Processes of Sucrose-Water and Non-Sugars
- 1998 Markwart Kunz, Südzucker AG, Mannheim/Ochsenfurt, Germany
Sucrose - Raw Material for Chemistry and Biochemistry
- 2000 Jean-François Thibault, Unité de Recherche sur les Polysaccharides, INRA, Nantes, France
New Ways to Add Value to Sugar Beet Pulp

Winners of the S.P.R.I. Industrial Technology Award

- 1998 Peter Rein, Tongaat-Hulett Sugar, South Africa
- 2000 Luis Rocha San Miguel Bento, RAR - Refinarias de Açúcar Reunidas, Porto, Portugal

S.P.R.I. Science Award Keynote Address

NEW WAYS TO ADD VALUE TO SUGAR BEET PULP

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INTRODUCTION

Sugar-beet pulp is the main by-product of the sugar beet industry; it is a waste which is abundant (the production in Europe is around 14 millions tons dry matter per year), available all year and cheap (around 110 Euros per ton). It is today mainly used in animal feeding but alternative uses to increase the value are currently being investigated (Broughton *et al.*, 1995; Hallarono and Berghäll, 1994 ; Vogel, 1991).

The Table 1 shows the chemical composition of the pulp. It contains a high amount of arabinose, galacturonic acid and glucose, which are the main sugars, and also lower amounts of proteins and ash.

Table 1 : Chemical composition of sugar-beet pulp (from Micard *et al.*, 1996, 1997a)

	% dry matter
Rhamnose	2.4
Arabinose	21.0
Galactose	5.0
Glucose	21.1
Xylose	1.7
Galacturonic acid	21.1
Methanol	2.0
Acetic acid	4.0
Ferulic acid	0.8
Diferulic acids	0.1
Proteins	11.0
Ash	4.0

This composition shows that sugar-beet pulp is particularly rich in polysaccharides: cellulose made of glucose (~20% of the pulp), and pectins (50% of the pulp) made of galacturonic acid, rhamnose, arabinose, methanol and acetic acid.

Recent analysis showed also the presence of phenolic acids, including ferulic acid and diferulic acids (dimers of ferulic acid) (Micard *et al.*, 1997a). These phenolics are born by the pectins (Ralet *et al.*, 1994).

Ferulic acid (Figure 1) is a bifunctional molecule. It can be bound through the acid group which can lead to ester linkages (with, for example, alcohol function of sugar residues in pectins) and through the phenol moiety which can lead to a variety of dimers. Indeed, dimers of ferulic acid (Figure 1) are present in the pulp, mainly the 8-O-4', 5-5', 8-5' and 8-8' dimers, the 8-5' derivative being the most abundant (Micard *et al.*, 1997a ; Oosterveld *et al.*, 1997). The isolation of dimers of ferulic acids is a strong indication of the existence of crosslinks between pectins in the beet cell walls.

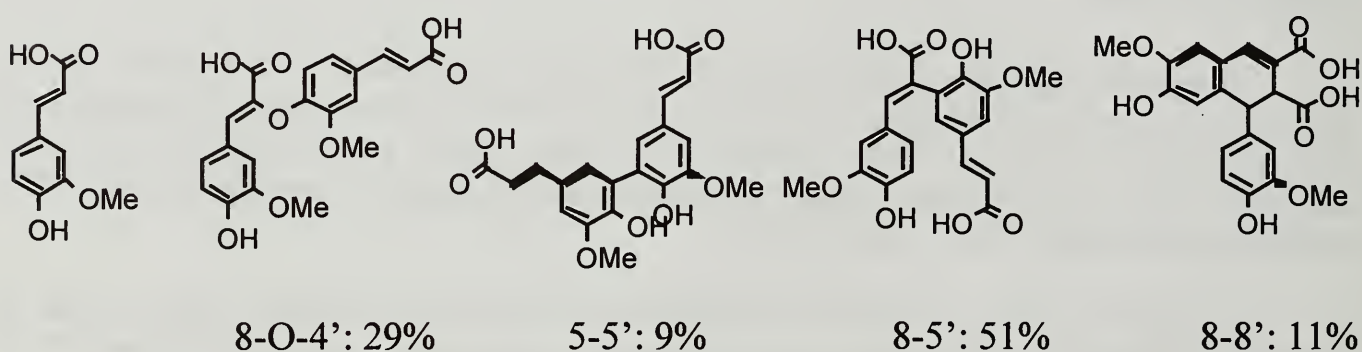


Figure 1 : Structure of ferulic acid and of the main dimers found in beet

A schematic model (Saulnier and Thibault, 1999) of the structure of beet pulp cell walls is proposed in Figure 2.

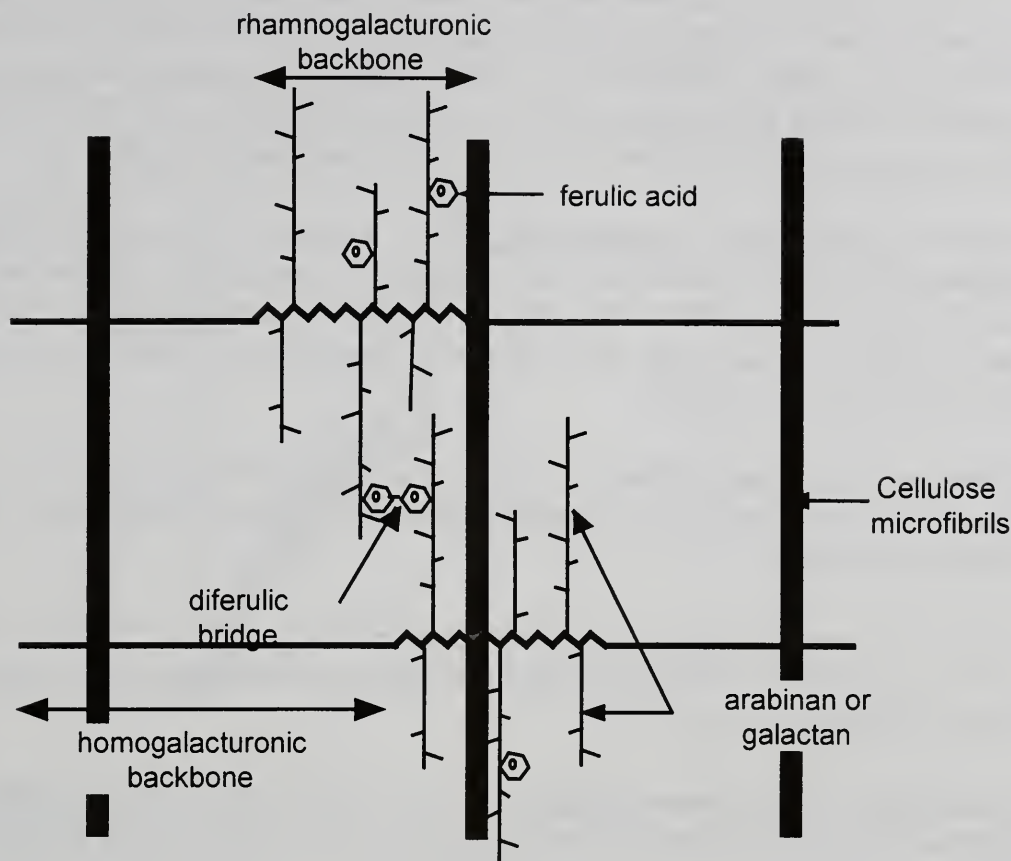


Figure 2 : Model for the sugar-beet pulp cell walls

Only cellulose microfibrils and pectins are represented because the amount of hemicelluloses (especially xyloglucans) is very low (Fares *et al.*, 2000) in these cell walls. Besides eventual ionic interactions through calcium bridges, covalent linkages involving diferulic acids may exist in pectins. The microfibrils of cellulose may be embedded in this pectic network.

Therefore the composition and the structure of the pulp indicated some ways to add value. Direct uses of the pulp can be proposed. As it consists mainly of cell wall polysaccharides, the use of sugar-beet pulp as a dietary fiber has been extensively studied. The pulp has physicochemical properties which allow its use as a functional fibre, without nutritional claims. The use of the entire pulp in the production of paper has also been suggested (Vaccari *et al.*, 1994). The extraction of polysaccharides (arabinans, pectins, cellulose) with valuable properties such as gelling, thickening, and stabilizing properties has also been proposed. The monomeric components (galacturonic acid, arabinose, rhamnose, ferulic acid) may be also valorized.

1. Beet pulp as source of dietary or functional fibre

The beet pulp must be processed before it can be used in food systems because it has a typical unpleasant flavour, may be too coloured and also may contain too high amounts of soil or sand (Bertin *et al.*, 1988 ; Michel *et al.*, 1988). Essentially physical treatments including cleaning, extraction, sieving and heating have been described (Tjebbes, 1988). The fibre may be finally milled to a given particle size from coarse to fine depending on its final use.

With special processing, it is possible to produce a dietary fiber, with an off-white colour and a neutral flavour, mostly devoid of ash and suitable for human food. Several processes have been patented (Thibault *et al.*, 2000). Beet fibres are today commercial products with a small market. These products contain more than 70% fibre consisting of a mixture of soluble and insoluble fibre (Thibault *et al.*, 1994).

This fibre has nutritional interests as well as functional interests (Thibault *et al.*, 2000). It is highly fermentable, due to the high amount of pectins but is able to decrease the transit time as well as the cholesterolemia.

Beet fibre has generally high water-retention capacities (around 30 mL/g), much higher than cereal fibres (< 5 mL/g). This could lead to satisfactory functionality as a dietary ingredient in food products (Thébaudin *et al.*, 1997).

Beet fibres behave as cation-exchange resins with a cation exchange capacity of about 0.5 meq/g (Thibault *et al.*, 2000). This ion-binding capacity is due to the presence of pectins. The relatively high value of cation exchange capacity has led to the idea to test beet pulp as a natural ion exchanger.

Indeed when compared to synthetic resins, beet pulp has the disadvantages to have a high swelling related to a high water retention capacity, a low exchange capacity, a poor recyclability. In contrast, beet pulp has the advantages to be biodegradable and to be of a very low cost. It is why beet pulp has been tested as a natural ion exchanger (Dronnet *et al.*, 1999).

The kinetics of the binding of the ions is a very rapid process since all the ionic sites may be occupied by ions in less than 15 minutes (Dronnet *et al.*, 1996, 1997). This is also an advantage for the pulp as an ion exchanger. The binding of a series of cations has been studied (Figure 3) and a very interesting selectivity scale was found: Cu is more tightly bound than Pb, than Cd than Zn than Ni and than Ca. This selectivity is due to the conformation of the pectins and is another advantage of beet pulp over synthetic resins.

The beet pulp may be therefore used to depollute metal-charged waters because the binding is very rapid, the selectivity is interesting and because heavy metals are very highly bound. It has been calculated that one ton of pulp is able to retain 26 kg of cadmium, 60 kg of lead and 20 kg of copper, for example (Dronnet *et al.*, 1999).

However, the problem still remains of how to treat the pulp after contamination with heavy metals. One possibility is to press the charged pulp and to burn the pressed pulp. Energy could be recovered together with a small volume of heavy metals.

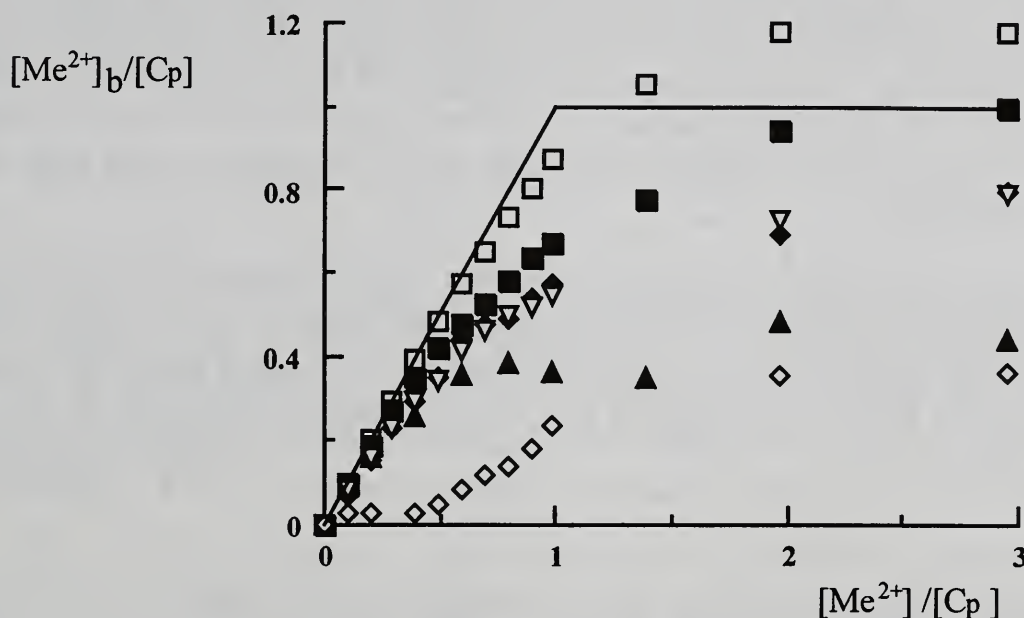


Figure 3 : Influence of the metal cation on the binding isotherms of sugar beet pulp (at 14.5g/l) in 0.1 M NaNO₃ at 25 °C at an initial pH ~7.2: (□) Cu²⁺, (■) Pb²⁺, (▽) Cd²⁺, (◆) Zn²⁺, (▲) Ni²⁺, (□) Ca²⁺; (—) stoichiometric isotherm

2. Beet pulp as a source of new pectins

A second way to valorize beet pulp could concern the extraction of polysaccharides. For example, arabinan may be extracted from the pulp and its potential as a fat replacer has been investigated (Broughton *et al.*, 1995). Cellulose may also be of interest (Chauvelon *et al.*, 1998 ; Dinand *et al.*, 1999) for producing films or stable suspensions.

Beet pectins have been investigated in detail. Indeed, apple pomace and citrus peels have until now been the only sources of commercial pectins which are used in industry mainly for their gelling and thickening properties. However, substitutes for these pectins are continuously investigated, and sugar-beet pulp could be a good candidate due to its high concentration of pectins (Rombouts and Thibault, 1986a, b).

High extraction yields of pectins can be obtained by heating the pulp in acidic conditions (Michel *et al.*, 1985). In these conditions, ferulic acid may remain on the side chains (Rombouts and Thibault, 1986a, b).

Beet pectins, as apple or citrus pectins, are made of "smooth" regions composed exclusively of galacturonic acids forming homogalacturonans, and "hairy regions" where the rhamnogalacturonic backbone carries neutral sugar side-chains. The "smooth" regions and the location of ferulic acid have been extensively studied and some specific features (Table 2) of beet pectins compared to apple or citrus pectins have been evidenced (Rombouts and Thibault, 1986a,b; Thibault *et al.*, 1991). In sugar-beet pectins, the galacturonic acid residues carry methyl esters (on the carboxylic group); however, the pectins are not very highly methylated, with a degree of methylation of about 50-60 instead of 70-80 in other plants. The backbone also carries acetyl esters. This substitution is quite rare and rather specific for beet (Voragen *et al.*, 1995). The location of the acetyl groups on the position 2 or 3 of the galacturonic acid is still uncertain. The degrees of acetylation of the beet pectins are generally of 25-30 and this is a very high value as compared with other pectins

In beet pectins as in other pectins, the side chains are mainly composed of arabinose and galactose forming arabinans, galactans and/or arabinogalactans (Guillon and Thibault, 1989 ; Guillon *et al.*, 1989). Beet pectins, however, have the particularity of bearing ferulic acid, which represents about 1% of the pectins. This phenolic acid esterifies some neutral sugars in the side-chains of pectins. More precisely, it is esterified for about 50% to the O-2 position of arabinose moieties and for 50% to the O-6 position of galactose residues (Ralet *et al.*, 1994 ; Colquhoun *et al.*, 1994).

Table 2 : Comparison of beet pectins with apple or citrus pectins

	Beet pectins	Apple/citrus pectins
Extraction yield (%)	10-15	15-25
Galacturonic acid (%)	60-65	70-75
Degree of methylation	50-60	70-75
Degree of acetylation	20-30	<5
Ferulic acid (%)	0.5 - 1.0	0.0
Gelation with calcium	No or low after deesterification	Yes after demethylation
Gelation with acid + sugars	No or low	yes
Oxidative gelation	yes	no

The beet pectins have therefore two main distinctive features when compared to conventional pectins from apple or citrus -- a high degree of acetylation and the presence of ferulic esters on their side-chains. The pectins from sugar-beet do not form gels in the usual conditions, i.e. neither with calcium nor with high sugar concentrations and acidic conditions. Acetyl groups are the most likely candidates for this inhibition (Pippen *et al.*, 1950) because they sterically hinder the association between chains required for the gelation.

The presence of ferulic acid on the side-chains can however be used for chemical crosslinking of beet pectins, the so-called oxidative gelation, which can lead to gel formation

(Rombouts and Thibault, 1986b; Rombouts *et al.*, 1987; Thibault and Rombouts, 1986 ; Thibault *et al.*, 1991). This is not the case of the apple or citrus pectins which are devoid of ferulic acid.

Crosslinking reactions through oxidation of these phenolic groups can be easily carried out. Enzymes, such as mixture of peroxide-peroxidase (Rombouts and Thibault, 1986) and laccases (Micard and Thibault, 1999) or chemicals such as persulfate (Thibault and Rombouts, 1986) can be used. Probably free radicals are involved (Thibault *et al.*, 1987) in the crosslinking process and in the formation of dimers of ferulic acids. It has been shown that the reaction increased the amount of the dimers, mainly the 8-5' and the 8-O-4' isomers (Oosterveld *et al.*, 1997).

The addition of these oxidants led to an increase in the viscosity of beet pectins in solution, or to gels depending mainly on the concentration of the pectin; 0.8% is the lowest concentration leading to gelation; stiffer gels can be obtained with concentrations of 1 or 1.5% (Thibault *et al.*, 1987, 1991). These gels are not reversible as they are based on chemical links and not physical links as in the other pectin gels. The crosslinked pectins can be therefore isolated by a drying process. The products thus obtained are powders; they do not dissolve in water but swell and they have remarkable water-absorption capacities (45-180 ml of water/ g of product; Thibault, 1986).

The swelling increases with decreased degree of crosslinking, which can be modulated for instance by the reaction time, is higher with monovalent than with divalent counterions and decreases when the ionic strength of the surrounding solution is increased (Table 3). These facts reflect the role of the screening of the fixed charges, leading to a reduction of the electrostatic repulsion and therefore a reduction of the expansion of the product (Thibault, 1986).

Table 3 : Water absorption (ml/g) of crosslinked pectins (at two degrees of crosslinking) as a function of the nature of the counterion and the ionic strength of the external solution

Ionic form	% of modified ferulic acid	
	66.7	74.6
H ⁺	55	45
Ca ⁺⁺	125	80
Na ⁺	180	95
Na ⁺ in 0.001M NaCl	160	100
Na ⁺ in 0.01M NaCl	125	70
Na ⁺ in 0.1M NaCl	75	45

Therefore, it is possible to extract a high amount of beet pectins but they have poor gelling properties in conventional conditions. However, the usefulness of the sugar-beet pectins was increased by the oxidative gelation and some new applications may be found as it is possible to increase the viscosity of their solutions or to produce gels. Furthermore, drying these gels gives new polymers insoluble in water but with very high water binding capacity. This property should lead to some new applications, as a cloud stabiliser in drinks, or as a water absorbing agent in sanitary products, for example.

3. The pulp as source of natural vanillin

A third way to add value to beet pulp could be to find uses for some of the monomeric constituents, such as galacturonic acid, rhamnose, arabinose (Vogel, 199), or ferulic acid (Thibault *et al.*, 1998). Ferulic acid is chemically very close to vanillin (Figure 4) and is a potential precursor of vanillin.

Vanillin is one of the most universally used aromatic molecules in the food, pharmaceutical or cosmetic industries (Thibault *et al.*, 1998). Two different types are commercially available: pure vanillin obtained by chemical synthesis, and vanilla extract obtained from vanilla pods. The extract contains 2-3% vanillin and other aromatic compounds. The world market for chemical vanillin is about 12,000 tons and the price is approximately 12 Euro/kg, whereas the world market for vanillin from vanilla pods is much smaller, around 40 tons. Moreover, vanillin from vanilla pods is much more expensive (55 Euro/kg of extract and 1800 Euro if the price is calculated per kg of vanillin in the extract). This high price is due to the complexity of the culture of vanilla, of aging and extraction. Nevertheless, the consumer demand for natural products is increasing more and more. In Europe, a flavour may be considered natural if it is obtained from natural products by safe biological processes including enzymic or microbiological means (Thibault *et al.*, 1998).

This definition was the starting idea for studies dealing with the production of natural vanillin from beet pulp. Thus, the challenge was first, to release ferulic acid from sugar beet pulp with safe enzymes, and secondly to find safe microorganisms able to process the bioconversion of ferulic acid into vanillin. The process was patented in 1991, which allowed the biotransformation of ferulic acid into vanillin by a strain of the filamentous fungi named *Pycnoporus cinnabarinus* (Gross *et al.*, 1991).

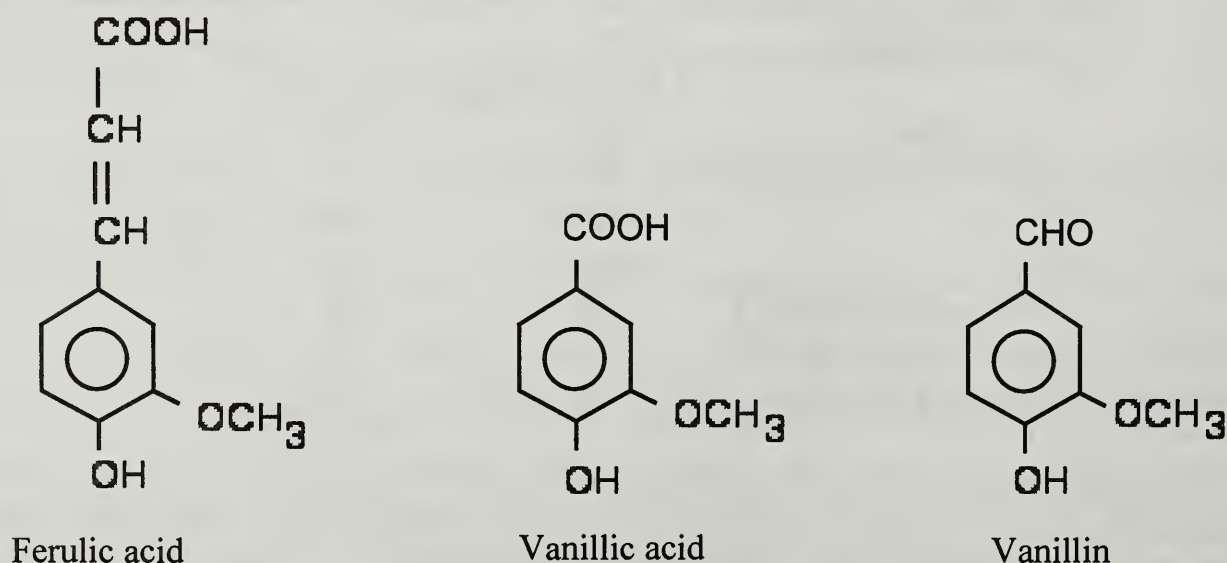


Figure 4 : Chemical structure of ferulic acid, vanillic acid and vanillin

The best conditions were to add 300 mg/L ferulic acid at day 3 and that induced a maximum concentration in vanillic acid of 40 mg/L at day 5 and the production of 64 mg/L vanillin at day 6.

In order to increase these very low yields, the metabolic pathways in *Pycnoporus* has been studied in detail. The analysis of the biosynthetic pathways showed that vanillic acid was an intermediate component, and that the strain presented three major divergent routes that lowered the yield of vanillin. Answers were found to inhibit these routes (Falconnier *et al.*, 1994).

The first one was a polymerisation of ferulic acid by a laccase activity. To avoid the polymerisation, a laccase deficient strain of *Pycnoporus cinnabarinus* was selected (Lesage-Meessen *et al.*, 1995). The second one was a decarboxylation of vanillic acid by an enzyme (vanillate-hydroxylase) producing methoxyhydroquinone. Addition of cellobiose in the culture medium limited the formation of methoxyhydroquinone. Cellobiose probably inhibited the enzyme responsible for the decarboxylation of vanillic acid (Lesage-Meessen *et al.*, 1997). The third one was a reduction of vanillin in vanillyl alcohol and was the response of the fungus to the toxicity of vanillin. Various ways were tried to avoid the reduction of vanillin. The best results were obtained by using a resin to adsorb specifically vanillin and not vanillic acid (Couteau and Mathaly, 1997; Stentelaire *et al.*, 1998). Therefore, vanillin can be easily and continuously removed from the broth and can be further extracted to get pure natural vanillin.

With the new strain cultivated in the presence of cellobiose, vanillin production reached 460 mg/L instead of 64 with the first strain and without cellobiose (Lesage-Meessen *et al.*, 1997). However, the yield of vanillic acid remained low and this step was still limiting. Therefore, another fungus able to achieve the biotransformation of ferulic acid into vanillic acid was looked for. A strain of *Aspergillus niger*, namely I-1472 was selected for its high ability to produce vanillic acid from ferulic acid (molar yield of about 90%). Thereafter, vanillic acid could be provided to *Pycnoporus cinnabarinus* which transforms it into vanillin reaching 560 mg/L, about 9 times more than the first value (Lesage-Meessen *et al.*, 1996). Thus, a system with two microorganisms which may efficiently transform ferulic acid into vanillin was designed. However, the enzymic release of ferulic acid from beet pulp has to be realised.

In order to obtain a "natural" ferulic acid, enzymes able to split ester bonds between ferulic acid and sugar moieties have been investigated (Thibault *et al.*, 1998 ; Wiliamson *et al.*, 1998). Two different feruloyl esterases were needed: one to release the ferulic acid linked to arabinose and another one to free the ferulic acid from galactose. Furthermore, it has been shown that these enzymes cannot work directly on polysaccharides but only on oligosaccharides.

This means that the polysaccharide backbone must first be degraded. This is achieved by a wide variety of enzymes including enzymes able to degrade the "hairy regions" (arabinanases, galactanases, rhamnogalacturonases, ...) as well as the "smooth regions" (polygalacturonases, pectinlyases, pectinmethylesterases, pectinacetyl-esterases...).

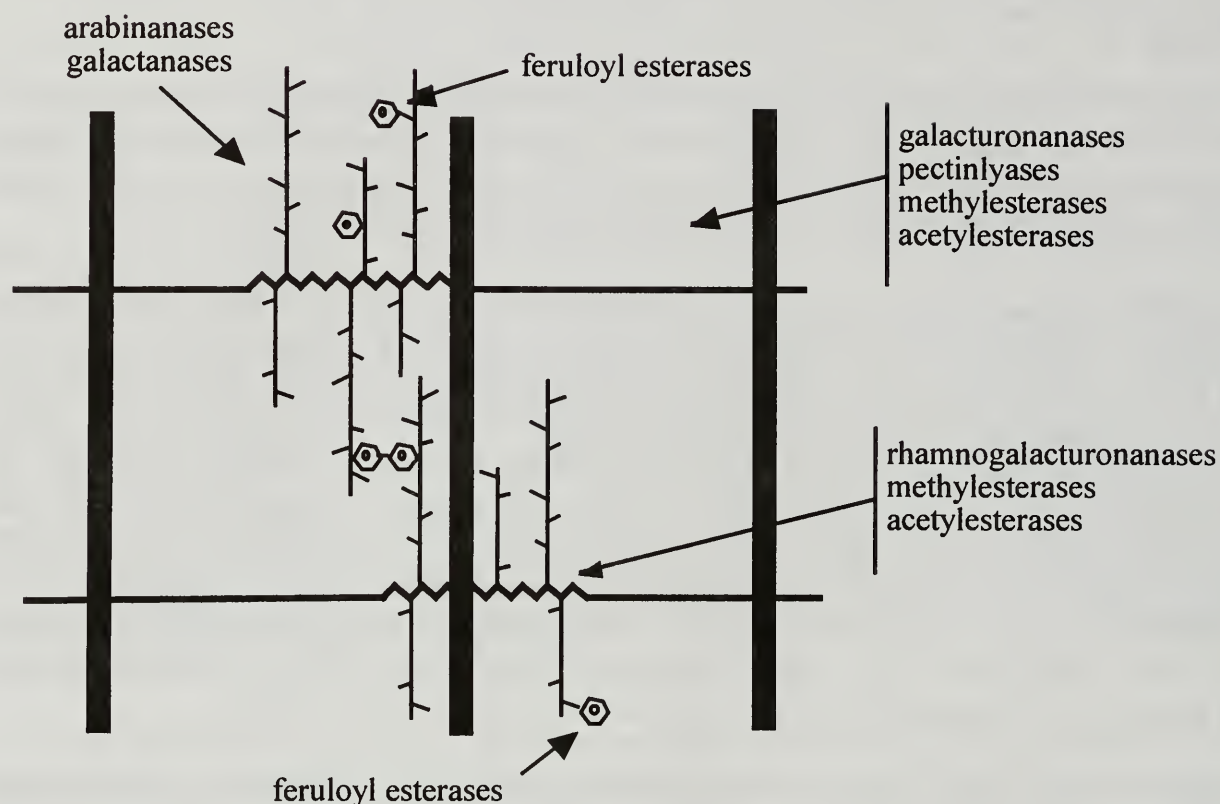


Figure 5 : The different enzymes needed for the degradation of beet pulp

The different activities necessary for this degradation can be found in various proportions in commercial preparations. Thus, a screening was carried out and some enzymic preparations have been selected (Micard *et al.*, 1994, 1996). With these preparations, acceptable yields in sugars were obtained, but the ferulic acid yields were always low, between 35 and 65%, showing that the amount of feruloyl esterases in all the preparations was a limiting parameter. In order to increase the release of ferulic acid, feruloyl esterases have to be added. This addition leads to an almost complete release of ferulic acid (Thibault *et al.*, 1998). Preparations devoid of cellulase activity may be selected in order to recover a cellulose-rich residue usable for further production of cellobiose by specific cellulases (Bonnin *et al.*, 1999). Indeed, cellobiose is important in our process because it hindered the methoxyhydroquinone pathway in *Pycnoporus cinnabarinus* leading to a decreased production of vanillin.

All these results allowed the design of a new process for the fungal production of vanillin from beet pulp. Ferulic acid is extracted from the hydrolysate and submitted to an *Aspergillus* strain in order to be transformed into vanillic acid, which in turn could then be purified, recovered as natural vanillic acid that is provided to *Pycnoporus cinnabarinus* in order to produce natural vanillin. The best results obtained with natural vanillic acid, laccase deficient

strain of *Pycnopus cinnabarinus*, cellobiose and resin were 560 mg of vanillin/L. The process is much more efficient since a 12-fold increase in the yield of vanillin was obtained (Lesage-Meessen *et al.*, 1996).

CONCLUSIONS

A lot of possibilities exist for adding value to beet pulp. It can be used as a source of dietary fibre; this fibre is now well documented and is sold by some companies. Beet pulp may also be used for remediation of water pollution. Beet pulp is also a potential source of pectin. It cannot compete with conventional pectin, such as apple or citrus pectin because it has not as good gelling power in classical conditions. But its specific manner of gelation may lead to products having potential applications which can justify its extraction. Beet pulp has also potential interest as a source of some very specific components. Ferulic acid can be one of them as it is the precursor vanillin. The valorisation of cellulose is also studied by various groups with the aim of obtaining new derivatives.

All these ways can be dependent in that an integrated valorisation scheme could be proposed in order to combine mass and niche uses. For example, figure 6 shows a possible integrated valorization of beet pulp.

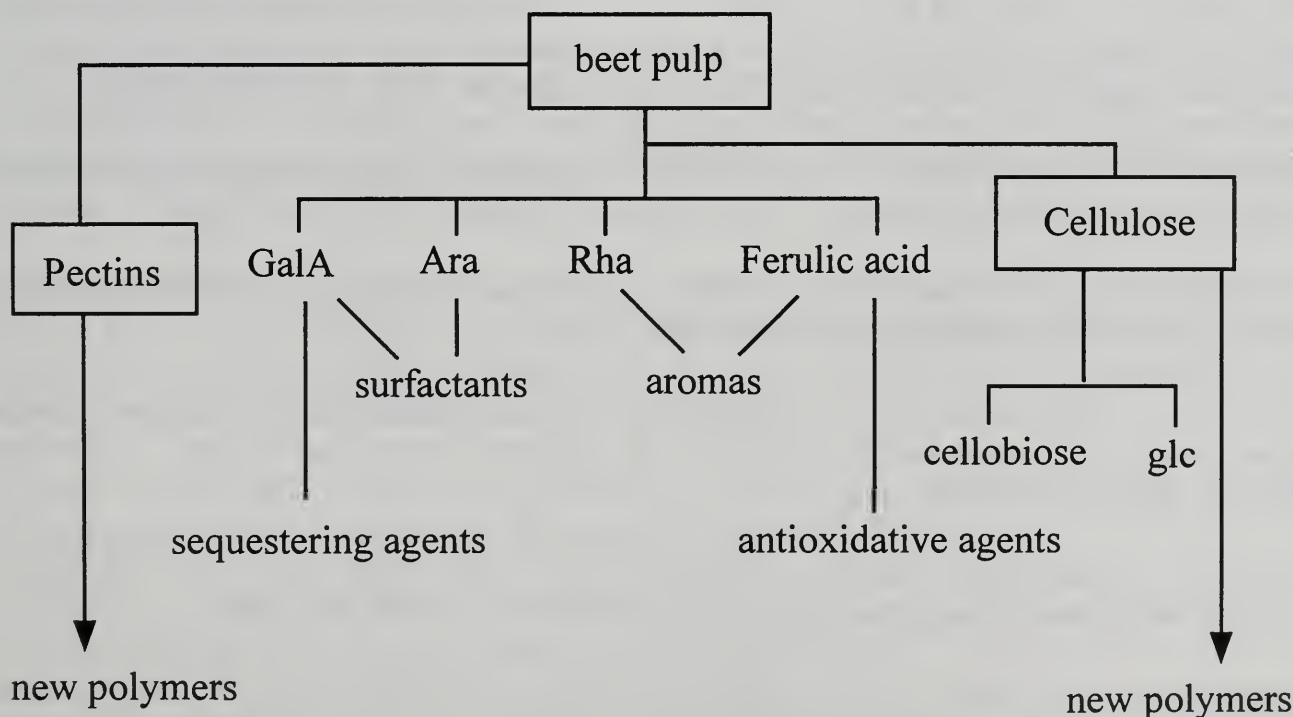


Figure 6 : Possible integrated ways of valorization of beet pulp

One way is to extract polymers: pectins can be extracted by acid and the cellulose residue may be used as a source of cheap cellulose and for the production of cellobiose. Another way may be to obtain pectic monomeric compounds by enzymic treatments, each of these

monomers having specific usages after eventual modification: sequestering agents, aroma precursor, surfactants. The cellulosic residue may in turn be valorized by the production of cellobiose or cellulose derivatives.

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VISION 2020: HOW GREEN CHEMISTRY CAN SHAPE THE FUTURE OF THE SUGAR PROCESSING INDUSTRY

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ABSTRACT

One of Society's biggest challenges as we enter the new millennium, is the elimination of industrial pollution. It is incumbent upon the research community to explore the inherent benefits of alternative industrial technologies which could reduce the associated environmental, and human health and safety concerns that accompany exposure to industrial pollution and which could lead to sustainable industrial practice. In a joint effort known as *Vision 2020*, staff members of the U.S. American Chemical Society, the Chemical Manufacturer's Association, the American Institute of Chemical Engineers, the Council for Chemical Research, and the Synthetic Organic Chemical Manufacturer's Association concluded "that the growth and competitive advantage of our industry depend upon individual and collaborative efforts of industry, government, and academe to improve the nation's R&D enterprise." One of the goals listed in the report from this group, *Technology Vision 2020: The U.S. Chemical Industry*, is to "enable the (chemical) industry to continue to lead in technology development, manufacturing and profitability, while optimizing health and safety and ensuring environmental stewardship."

In order to develop a comprehensive international agenda for pollution prevention in industry, we must change the way people think about industrial processes. Green chemistry, engineering, and technology must be integrated into the science and education curriculum at all levels of education so students are exposed to the problems and can learn how to approach solving them. This paper will discuss the concepts of the new paradigm of Green Chemistry, the role of chemists in sustainable industry, and the impact on the sugar processing industry. Aspects of the chemical and agriculture industries which will play major roles in future sustainable technologies will be highlighted.

INTRODUCTION

The 20th century heralded the development and production of vast amounts of chemical products including antibiotics, fertilizers, pesticides, polymers, and CFCs. While many of these products have resulted in the betterment of our living conditions, certain aspects of their manufacturing processes have produced deleterious results. In the past, the societal perception

of chemistry and the chemical industry centered on innovations resulting in medical breakthroughs and modern conveniences. More recently, with the rapidly expanding chemical industry, that perception has changed, and many perceive the industry as a major contributor towards air, land, and water pollution.

To regulate waste management issues and problems, a profusion of environmental regulations has enforced stringent controls on the emission, discharge, and disposal of chemicals associated with manufacturing processes. The end result of these regulations has made an impact on manufacturing by forcing chemical companies to enact standards to control the amount of gas they release into the air, liquid waste they release into the water, and solids they defer to land disposal.

Chemistry plays an important role towards reducing the amount of waste that is non-recyclable. This can be achieved via developing alternative means to produce the product, focusing on "Green Chemistry" and reducing environmental risk by reducing hazards associated with particular manufacturing processes.¹ From the Green Chemistry standpoint, it is better to prevent waste than to treat or clean up waste after it is formed. In addition, synthetic methodologies should be designed to produce optimum amounts of product and generate substances that possess little or no toxicity to human health and the environment. These goals can be realized through the development of new technologies for industrial pollution prevention.

GREEN CHEMISTRY

The characterization of environmental problems follows a rather simple equation, a chemical of some hazard is released into the environment in some quantity, which produces an exposure. These two factors equate into an environmental risk. The focus on reducing the environmental risk (and the focus of almost all environmental regulations) has traditionally been reducing the exposure. The problem with focusing on exposure is that it is costly and can possibly fail. If exposure limits fail, the risk remains.

Green Chemistry works toward reducing the hazard and thus the environmental risk; it cannot 'fail'. Green chemistry involves designing chemical products and processes that reduce or eliminate the use and/or generation of hazardous substances.¹ It also involves a fundamental shift in the way that science views chemical design and synthesis. Chemists at the design stage are now taking into consideration the entire range of human health and environmental effects of any proposed chemical or process and are working toward minimizing those impacts.

Green Technology is research and development of new processes and new products that are environmentally benign, thus eliminating toxic waste byproducts generated during manufacturing as well as developing new environmentally-safe products. In the past the factors that have influenced chemical design and synthesis have been the number of synthetic steps, cost and availability of raw materials, and product yield. With a focus on design, the yield of the synthesis must equal the feedstock that is needed. The factors influencing chemical design and synthesis from a Green Chemistry aspect thus include these same factors, but also include chemical handling costs, waste treatment/control/disposal costs, and regulatory compliance costs. With these new factors, the design must balance yield with feedstock, regulatory compliance,

disposal, liability, and treatment. For example, the vast majority of industrial chemical processes that are in use today were developed over 20 years ago. The costs associated with these processes have changed considerably over this time period. Industry spent \$115 billion in 1992 on waste treatment, control, and disposal. It was estimated at that time that it would cost as much as \$700 billion to clean up existing hazardous waste sites. These costs, and the costs associated with regulatory compliance, are rising.

P. Anastas and J. Warner have written a series of books outlining the principles and practices of Green Chemistry. One such book *Green Chemistry: Theory and Practice*,^{1a} which is heavily referred to in this paper, defines and establishes the principles of Green Chemistry. Also recently, the Royal Society of Chemistry has initiated a journal entitled *Green Chemistry* (<http://www.rsc.org/is/journals/current/green/greenpub.htm>) that publishes the latest developments in this area.

The 12 Principle of Green Chemistry¹ can be summarized as follows. It is better to prevent waste than to treat or clean up waste after it is formed. Wherever practicable, synthetic methodologies should be designed to use or generate substances that possess little or no toxicity to human health and the environment. Synthetic methodologies should be designed to maximize the incorporation of all materials used in the process into the final product. The raw materials used in these methodologies should be renewable, rather than depleting, wherever technically and economically practicable. The catalytic reagents used in the synthesis should be superior to stoichiometric reagents. The use of auxiliary substances in the synthesis should be made unnecessary wherever practicable, and in cases where they are necessary, should be innocuous. The products from any synthesis should be designed to achieve efficacy of function while reducing toxicity. When the chemicals are at the end of their functional life, they should be environmentally benign. The substances used during the synthesis process should be chosen so as to minimize the potential for chemical accidents resulting from releases, explosions, and fires. The analytical methodologies used should be developed and utilized to allow for real-time, in-process monitoring and control in order to reduce or eliminate the formation of hazardous or unwanted substances.

U.S. NATIONAL GREEN CHEMISTRY INITIATIVES

Several programs at the national level in the U.S. have been initiated over the past decade to promote the ideals of Green Chemistry and sustainable development. These programs range from R&D-oriented programs to stimulate innovative graduate education and research, to direct grants to industries willing to develop new green technologies.

The Environmental Protection Agency (EPA) has both a Green Chemistry Program (<http://www.epa.gov/opptintr/dfe/greenchem/index.html>) and a Sustainable Technology Division (<http://www.epa.gov/ORD/NRMRL/std/>). The mission of the Green Chemistry program is to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacturing, and use of chemical products. The Sustainable Technologies Division conducts research in the area of Green Chemistry in order to advance the understanding, development, and application of technologies and methods for prevention, removal, and control of environmental risks to human health and ecology.

The Department of Energy (DOE-<http://www.doe.gov/>) Office of Industrial Technologies (OIT-<http://www.oit.doe.gov/>) is an example of a program designed specifically for industry. OIT creates partnerships among industry, trade groups, government agencies, and other organizations to research, develop, and deliver advanced energy efficiency, renewable energy, and pollution prevention technologies for industrial customers.

One of OIT's more interesting programs is their Industries of the Future program (<http://www.oit.doe.gov/industries.shtml-iof>). Initially nine of the most energy intensive industries were selected to participate in industry-led programs to set a vision for reduced energy use consumption and environmental impact and to develop an R&D technology roadmap for its implementation. The initial nine industries within this program included agriculture, aluminum, chemicals, forest products, glass, metal casting, mining, petrochemicals, and steel.

Each industry began the process with the setting of a vision, where industry leaders, trade group representatives, and a few university representatives developed a comprehensive vision statement for where the industry should be by the year 2020 (<http://www.oit.doe.gov/tools.shtml>). The vision process was followed by a series of technology workshops (still ongoing in several instances) to develop R&D roadmaps needed to achieve the vision. These technology roadmaps^{2a,2c,3} have already been used by several funding agencies to prioritize research needs. Within DOE-OIT itself, several Request for Proposals to industry partners have been issued, and several million dollars in research funding have been granted to industry.

The Industries of the Future goals are carried out at the state level through the DOE-OIT States Industries of the Future program (<http://www.oit.doe.gov/states/statesiof.shtml>), where the advanced industrial technologies are implemented. The Center for Green Manufacturing (<http://bama.ua.edu/~cgm>) at The University of Alabama (<http://www.ua.edu>) is leading Alabama's Industries of the Future program for the Chemical Industry. The CGM is focused on developing green technologies that will lead to pollution prevention in the manufacturing sector.

In this paper, we will focus on two of the largest industry segments: Chemicals (<http://www.oit.doe.gov/chemicals/page12.html>) and Agriculture (<http://www.oit.doe.gov/agriculture/page9.html>). As will become evident below, there are many synergies to be exploited in the development of sustainable industrial between these two powerful components of the U.S. economy.

TECHNOLOGY VISION 2020, THE U.S. CHEMICAL INDUSTRY

The goals developed by the chemical industry and now known as *Technology Vision 2020* (<http://www.ccrhq.org/vision/index.html>), contain the old concepts: "to ensure that the Chemical Industry maintains a lead in the areas of development, production, and profit", but also a new concept: that this be done "while optimizing health, safety, and environmental stewardship".² The Technology Roadmaps which arose from the Vision 2020 process emphasized the development of new catalysts to prepare economical and environmentally-safe processes with lower life cycle costs, and improving the performance of biocatalysts and biochemical

processing. Additionally, the roadmaps stressed the need for alternative reaction media and *renewable raw materials* to alleviate the reliance on oil-based feedstocks.

PLANT/CROP BASED RENEWABLE RESOURCES 2020, THE AGRICULTURE INDUSTRY

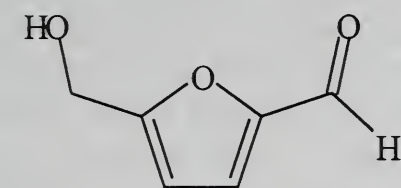
The Agriculture vision statement (<http://www.oit.doe.gov/agriculture/page1.htm>) appears to dovetail with several aspects of the Chemical Technology Roadmaps. The Agriculture Industry sees itself providing economic growth through the development of plant/crop-based renewable resources that are viable alternatives to the diminishing fossil fuel-based raw materials many chemical companies now rely on.

The technology roadmaps for agriculture developed a list of several key opportunities, goals, and priority areas.³ Key opportunities include R&D in *basic plant science*, where one could alter plants to produce specific targeted molecules (the idea of a living plant as a miniature chemical plant); *production*, where unit costs must be lowered for renewables to be competitive; *processing*, where improved separations are needed to lower energy utilization and waste production; and *utilization*, where improving renewable material performance is a target. These opportunities were prioritized as follows: engineering metabolic pathways to enhance yields of target compounds; design, production, and handling of dedicated crops; new separations technologies to handle heterogeneous plant materials; determination of structure-function relationships for plant constituents; and the development of rural areas for support production, for marketing, and for increased utilization of plants.

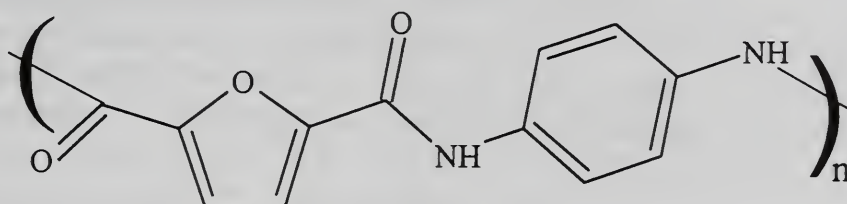
Major contributions of the agriculture industry to the chemical industry may be realized through the engineering and processing of basic building blocks for manufacturing which can produce quality consumer goods and recycling of starting materials. From the early 1980's on, there has been an increase in the contribution to the U.S. economy by agricultural products, as well as a steady increase in the dependence on agricultural resources for the country's chemical and material needs.³ While many assume that a carbohydrate economy can replace the current petrochemical economy at some future point (<http://www.carbohydrateeconomy.org>), specific examples of cost-effective renewable alternatives are already beginning to show up in the marketplace.

When the total life cycle costs of bioproduced raw materials are considered, they often are substantially lower than petrochemical based materials. For example, the cost to use d-limonene is considerably lower than the traditional organic solvent 1,1,1-trichloroethane (TCE) when considering the higher disposal costs and much higher post-disposal liability cost of TCE.³

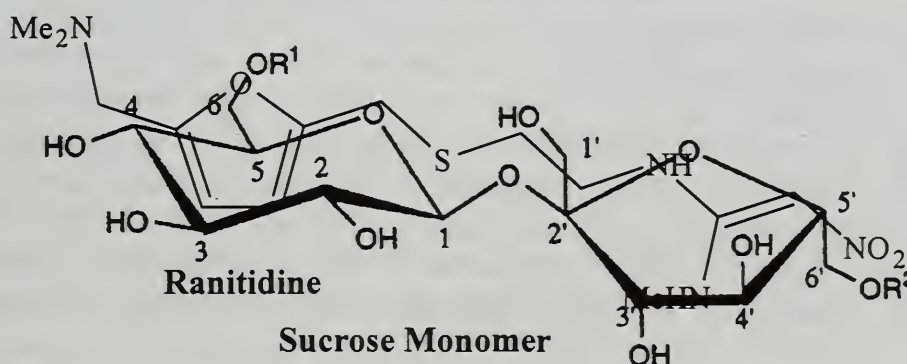
One of the few 'petrochemicals' readily accessible from renewable resources and a key substance linking carbohydrate chemistry and petrochemicals is 5-hydroxymethylfurfural (HMF).⁴ Furfural has traditionally been used in synthetic resins, electrical insulating materials, coating materials, furacilins, and as an anti-corrosion material. By derivatizing HMF to the dicarboxylic acid, the molecule can then be used to replace adipic acid or terephthalic acid in the production of an analog of Kevlar.⁴ HMF can also be used to form Ranitidine, an anti-ulcer drug with over one billion dollars in annual sales.^{4,5}



5-hydroxymethylfurfural



An analog of Kevlar



Ranitidine

Sucrose Monomer

Another molecule that can be a link between the agriculture and chemical industries is sucrose, which can be used in the preparation of thermo-reversible sucrogels. The gels formed from this monomer are degradable and suitable for controlled drug delivery. Also by varying the R group the hydrophobicity of the gel can be controlled. Sucrose can be derivatized into isomaltulose which can be further derivatized to give non-ionic easily biodegradable detergents and it can be polymerized to yield a highly hydrophilic polymer, which can be used as a non-ionic surface active agent.⁶ The isomaltulose can also form GPA-lactones which can be derivatized to yield compounds that possess liquid crystalline properties to be used as detergents.

These are but a few examples of a growing number of links between renewable raw materials and the chemical industry. There are, however, still major barriers that must be overcome in order to make the process of using renewable resources efficient; including gaps in plant science, plant/crop production, processing, and utilization.^{3,7} In plant science, an understanding of how the target plants work, plant genomics, the effects of certain enzymes on the cells of the plant, and plant metabolism and composition must be obtained. In the area of production, unit costs must be lowered while yield is increased in order to compete with today's market. It will be extremely important that the products be of consistent quality and easily separated to ensure recyclability.

The utilization of these new materials can be separated into two areas, one for the materials themselves and one for the demand placed on the products that are made from processing. The materials used must be economical with high functionality and performance to ensure stability. The demand for products produced by any new methods will be driven by reasonable value at a low price. In addition, performance of the product must be comparable to what is currently on the market, and if a completely new product is made, a market for this new product must be developed.

To meet the needs for alternate products and technologies of tomorrow, multidisciplinary research programs should be developed now. A combination of government, federal and local government, academia, and industry is needed to lead R&D towards renewable resource-driven methods of chemical and consumer goods production.³ The agriculture industry should play a major role in this process.

SIGNIFICANCE OF GREEN CHEMISTRY TO THE SUGAR PROCESSING INDUSTRY

The sugar processing industry does not normally bring to mind images of pollution and waste; however, several possible areas of environmental concern need to be addressed by the industry before they reach problematic proportions. Increasingly, the sugar processing industry is coming under fire from environmental advocates and agencies. Recently, a U.S. sugar processing plant received fines in excess of \$3 million for mishandling of hazardous waste. Also, a Federal District Judge issued a court order requiring cleanup of sugar industry pollution in the Florida Everglades.⁸ These instances stand out as challenges to the sugar processing industry to begin exploring ways to make sugar processing even more environmentally friendly.

As within the chemical industry, the sugar processing industry must realize that waste is increasingly unacceptable and strategies for dealing with it must be considered. In an article addressing the significance of Green Chemistry to small- and medium-sized enterprises, C. Drew outlined proposed approaches to pollution prevention⁹ which included: a) effluent treatment; b) better process control and recycling; c) better process design; and d) alternative processes. The first two approaches address pollution prevention by way of cleaner effluent and less effluent, but the last two approaches are considered the heart of Green Chemistry. These approaches challenge industry to reevaluate processing. Better process design can achieve reduced waste, while new alternative processes may be able to eliminate waste altogether.

The Sugar Processing Industry should also be willing to use wastes as feedstocks or sustainable resources for other industries. For example, Brazil has been creating ethanol from sugar to power automobiles for some time.¹⁰ Recently, the beet sugar industry has focused attention on the recovery of value-added products such as betaine from waste beet molasses.¹¹ (Betaine is the most abundant nitrogen-containing compound found in beet molasses.¹²)

The 12 Principles of Green Chemistry¹ can provide the sugar processing industry with a guide to developing new processes and R&D programs which address the environmental issues/concerns of the industry. The representative examples provided below are but two areas which illustrate identifying and solving possible environmental challenges within the Sugar Processing Industry.

Example of Materials Changes: Elimination of Lead in Polarimetry

Lead subacetate has been used routinely to determine the purity of optically active sucrose solutions.¹³ The lead is used as a clarifying reagent prior to measuring optical activity. A U.S. sugar factory was fined over \$3 million dollars for mishandling hazardous chemical waste, specifically lead. The EPA had determined that the lead treatment waste cannot be discarded without proper treatment.¹⁴ Alternatives to this technique were found including clarification using aluminum salts or Membrex ultrafiltration,¹⁵ but were not consistently implemented. While the lead subacetate clarification process has been replaced in the U.S., the rest of the world has not followed suit.

Example of Process Changes: Cane Juice Analysis by Near Infrared

While the above example is illustrative of a positive change in environmental impact, it is often the case that entirely new procedures can be found which outperform 'tried-and-true' methodologies, both economically and environmentally. A good example of this is the development of Near Infrared (NIR) techniques to analyze cane juice as reported by T. Johnson at SPRI-2000 in Porto, Portugal.¹⁵ The NIR analyses can be performed without the harsh chemicals of the polarimetry methods and with reduced labor costs. The method is also much simpler and less time consuming than traditional analyses. With appropriate modification, NIR should be applicable to in-line monitoring, thus reducing even further the time demand on personnel and processes¹⁵ (and thus meeting the 12th principle of Green Chemistry¹).

Near Infrared is finding additional utilization in the food industry. Recently Ding and Xu from the University of Hong Kong reported the use of NIR for the determination of adulteration in beef products.¹⁶ Again the NIR technique was lauded for its ability to allow rapid screening and to eliminate the drudgery of tedious, technically-demanding analyses.

THE UNIVERSITY OF ALABAMA CENTER FOR GREEN MANUFACTURING

"There does not exist a category to which one can give the name applied science. There are science and the application of science, bound together as the fruit to the tree which bears it."

Louis Pasteur, 1871 (translated from Review Scientifiques)

In order to develop a comprehensive national agenda for pollution prevention in industry, the way people think about industrial process must change. Green technology must be integrated into the science and engineering curriculum at all levels of education so that students are exposed to problems and can learn how to approach solving them. The University of Alabama is developing a comprehensive R&D Center to integrate new environmentally benign technologies with a new paradigm of educating chemists and engineers. The Center for Green Manufacturing maintains a research mission to discover and to develop a molecular level understanding of industrial processes and products that will allow the redesign of manufacturing technologies to

prevent pollution and save energy. This mission will be accomplished by utilization of interdisciplinary scientific and engineering problem solving teams for the research and development of green technologies. These teams are given opportunities to gain expertise in assigned fields and to collaborate directly with industry to solve problems and find immediate applications for green technologies. Also the CGM allows for opportunities for the teams to gain an interdisciplinary, team-oriented education in the tenets of Green Chemistry.

R&D in the Center for Green Manufacturing

Separations are ubiquitous in every industry, yet are rarely considered when determining the environmental impact of a manufacturing process. Thus, one area of opportunity for new chemical science and engineering technology which will help meet the goals of *Technology Vision 2020* is the development of new separations technologies that eliminate the use of flammable, toxic volatile organic compounds (VOCs) as solvents.¹⁷ Used in conjunction with, or instead of appropriate current manufacturing processes, such technologies would help to prevent pollution and increase safety.

Traditional solvent extraction employs partitioning of a solute between two immiscible phases, typically an organic solvent and aqueous solution.¹⁸ The ability to utilize a number of different diluents, extractants, and aqueous phases makes solvent extraction a powerful separations method possessing a number of favorable characteristics including rapid extraction kinetics for many separations, the adaptability of the method to a wide variety of solutes, and back extraction or stripping of the solute and recycling of the solvent and/or diluent. Further, liquid/liquid extraction is capable of large volume throughput and is amenable to large-scale separations, and can be engineered for high selectivity and efficiency by the use of multistage contactors.

Liquid/liquid extraction has often been a favorite choice for the development of separations processes, and typically this involves the use of an organic solvent into which the organic molecules partition or in which the extractant resides for the complexation and removal of metal ions from an aqueous phase. A characteristic of many VOCs that has been exploited in this regard is their water immiscibility that induces the formation of a two-phase system when contacted with water. As over 90% of hazardous waste is aqueous,¹⁹ considerable emphasis has been placed on processes that provide efficient means for solute separations from liquid media. Liquid/liquid extractions employing an organic solvent have become a common industrial separation process due to the ability to fine-tune both the hydrophobic and complexing properties of the extracting phase through the use of various organic solvents available. Worldwide usage of solvent at a cost of 5 billion dollars indicates the large quantity of VOCs consumed per annum.²⁰

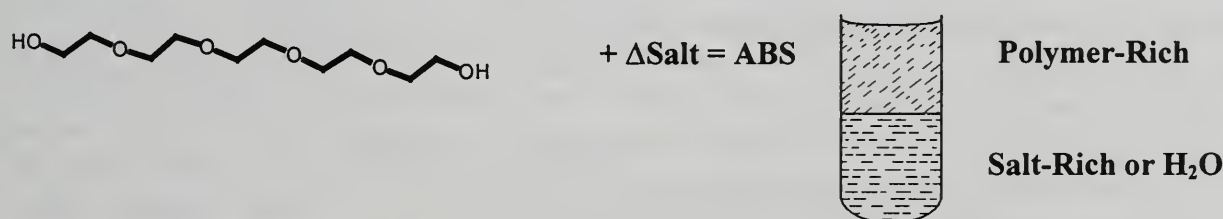
Despite the widespread use of organic diluents, the abbreviation VOC has become synonymous with a plethora of social, economic, and ecological hazards. (When the diluent is coupled with a highly selective extractant the cost of the solvent system can become very expensive, not to mention the costs of safely designing a system to operate with a volatile or flammable diluent and the high costs of disposal.) With the increased emphasis on the adoption of clean manufacturing processes and environmentally benign technologies, such use seems increasingly anachronistic. It is thus worth exploring the inherent benefits of alternative

technologies to replace VOCs and reduce the associated health risks, volatility, environmental, and human health and safety concerns that accompany exposure to organic solvents. In environmental remediation and hazardous waste treatment, the generation of additional toxic or hazardous waste, doesn't present itself as a logical solution to the problem.

Several separations technologies, some of which have been intensively studied and others which are only now getting attention in the separations community, have the potential to reduce VOC use in industrial application. Two such technologies under active investigation at the CGM include the use of environmentally-benign polymer systems¹⁷ and ionic liquids (IL).²¹

Aqueous Biphasic Systems (ABS)

Aqueous biphasic systems form upon the admixture of certain water-soluble polymers or polymers and salts above critical concentrations, and thus represent liquid/liquid extraction systems whose nature is entirely aqueous.^{17,22-38} ABS have been studied for some time for gentle separations of proteins or other biomass,³⁹⁻⁵¹ however, projects in the CGM laboratories have also demonstrated that ABS are suitable for the extraction and separation of metal ion species.^{26,27,30,37} These systems warrant consideration for the development of environmentally benign wet extraction processes, a role which is well outside, and rather different, from their current rather limited application in biotechnological separations.^{23,40,46}



Aqueous biphasic systems retain all of the practical advantages of liquid/liquid extraction and also have a number of unique advantages due, in large part, to their aqueous nature. Polyethylene glycol (PEG)-based ABS are virtually nontoxic and nonflammable. All components are commercially available in bulk quantities, are inexpensive, and the systems have reasonable phase separation characteristics that can even be used with traditional solvent extraction equipment. In addition, the PEG-rich phases in PEG-ABS appear to be tunable; their phase characteristics can be changed to match the hydrophobicity and water content of a number of organic solvents.

ABS have been criticized for some applications because of the necessity to strip into a salt solution so that a two-phase system is maintained. Difficulties with stripping, however, have been overcome by successfully adapting PEG-ABS to solid chromatographic separations processes via covalent attachment of monomethylated-PEG to an inert polystyrene-divinylbenzene backbone (forming Aqueous Biphasic Chromatographic (ABEC) resins).^{32,35} Thus, in column chromatographic mode, stripping can be accomplished simply by elution with water.

Although attachment of PEGs to a solid support is not new, by relating the resin behavior directly to liquid/liquid ABS,²⁷ we have been able to utilize these resins in unique separations technologies. Importantly, these tunable, affinity adsorbents can be stripped simply by elution

with water. Given the current emphasis on Green Chemistry and the desire to prevent pollution by redesign of industrial processes, ABS and ABEC represent an economical avenue for 'clean' separations. Three patented technologies⁵²⁻⁵⁴ offer evidence of the applicability of these technologies to a wider industrial sector. Successful ABS and ABEC R&D has included the following:

- $\text{TcO}_4^-/\text{MoO}_4^{2-}$, $\text{ReO}_4^-/\text{MoO}_4^{2-}$, and $\text{ReO}_4^-/\text{WO}_4^{2-}$ separations for radiopharmacy and hydrometallurgy^{33,35}
- Separation and recovery of TcO_4^- from Hanford tank wastes^{35,55,56}
- Separation and recovery of food coloring dyes or textile dyes⁵⁷
- Separation and stripping of metal halide complex anions for hydrometallurgy applications^{58,59}
- Adaptation of liquid/liquid PEG-ABS to a solid-supported chromatographic mode^{32,35,60}
- Proving that ionophores capable of metal ion recognition can be used in PEG-ABS^{35,61}
- Development of iodine specific resins⁶²

Ionic Liquids (IL)

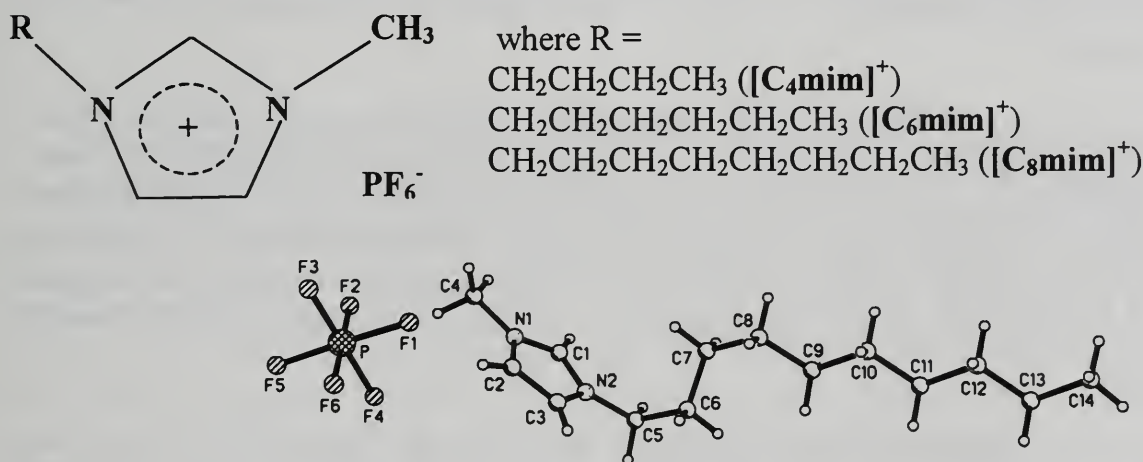
One of the most promising areas of research in new green technologies is the application of neoteric solvents, a category which includes supercritical CO_2 and ionic liquids (IL). One of the least explored and most promising approaches is the use of IL, and perhaps as a result of the compelling need for industry to consider the reengineering of entire processes, IL have begun to receive worldwide academic and industrial attention⁶³⁻⁶⁸ as replacements for organic solvents in catalysis (where the IL can act as both catalyst and solvent),⁶⁹ synthesis (where IL have unique solvent effects which limit conventional solvation and solvolysis, may enhance reaction rates and selectivity, and reduce side reactions),⁷⁰⁻⁷³ and separations processes (where moisture stable, water immiscible IL have been shown to partition a wide variety of aryl organic molecules from water and early results lead to the expectation that applications may be developed on the basis of traditional solvent extraction principles),^{21,74,75} in addition to their well known role in electrochemistry (where IL can have large electrochemical windows, high conductivities, and limit solvolysis).⁷⁶⁻⁷⁸

What Are Ionic Liquids? Ionic liquids are composed of large, asymmetric, organic cations and various anions that produce non-volatile and non-flammable liquids capable of solubilizing a variety of solutes.⁶⁷ These ionic solvents are composed entirely of ions, and, in comparison, strongly resemble ionic melts which may be produced by heating metallic salts such as sodium chloride to high temperature (*e.g.*, NaCl to over 800°C),⁶⁵ but are liquid at much lower temperatures. (A working definition for the distinction between an IL and a molten salt of melting points less than 150°C has recently been suggested.⁷⁹) IL are good solvents for a wide range of inorganic, organic, and polymeric materials. The composition of IL may be adjusted enabling control of their acidity and basicity. IL are now known which are both stable to moisture and are immiscible with water, thus enabling their use in liquid/liquid extraction from aqueous media.^{21,76-78} In addition, many IL are relatively undemanding and inexpensive to manufacture. (We have recently put together a short PowerPoint presentation reviewing this data on the web at URL: <http://bama.ua.edu/~rdrogers/webdocs/RTIL/index.htm>.)

Many IL are liquids over a wide temperature range (for some this range may exceed 300 °C) and IL with melting points as low as -96 °C are known.⁶⁴ The constituents of IL (being ionic) are constrained by high coulombic forces and thus, exert practically no vapor pressure above the liquid surface. These features, and the potential to reduce pollution in industrial processes, have led to current investigations of IL as alternative reaction media for a variety of applications that use organic solvents.⁸⁰⁻⁸²

Ionic Liquids for Novel Separations. IL can add to the growing toolbox of green separations technologies, and separations scientists are now starting to look at these neoteric solvents for VOC replacement.⁶⁴ Although much work remains to be done, IL show promise for novel liquid/liquid separations strategies.^{21,80}

The low melting nature of IL can be engineered by the choice of anionic and cationic species to produce salts with low lattice energies. The majority of IL studies reported in the literature to date have utilized large, asymmetric organic cations to produce this effect. The most common examples include *N*-alkylpyridinium and 1-alkyl-3-methylimidazolium (Rmim) cations in which the alkyl group may be varied to fine-tune the physical properties of the RTIL. For example, notable changes in melting point are observed as the length of the alkyl chain increases in [Rmim][PF₆] ionic liquids; the ethyl derivative ([C₂mim][PF₆]) melts at 58-60 °C⁸³ while at room temperature, the butyl (mp = 4 °C), hexyl (mp = -78 °C), and octyl (mp = -72 °C) derivatives are liquids.⁸⁴ When R is increased to the decyl group ([C₁₀mim][PF₆]), the salt is a solid at room temperature (mp = 37 °C).



1-Decyl-3-methylimidazolium Hexafluorophosphate ([C₁₀mim][PF₆])

The choice of cation need not be limited to pyridinium or imidazolium salts and the range of potential cations is exceedingly large. For example, asymmetric tetralkylammonium or phosphonium salts may also form IL. Choice of cation, their modification (*e.g.*, fluorinated or chiral alkyl groups), and the determination of chemical and physical properties offers a fertile field of research, where the possible permutations may only be limited by imagination.

Recently, IL have been identified in which the anion is not only stable to moisture, but imparts water immiscibility as well, hence rendering them capable of forming a two-phase system with aqueous media.^{64,76,83} The anions reported in this category include PF₆⁻, BF₄⁻,

triflate (CF_3SO_2^-), nonaflate ($\text{CF}_3(\text{CF}_2)_3\text{SO}_2^-$), bis(triflyl)amide ($(\text{CF}_3\text{SO}_2)_2\text{N}^-$), trifluoroacetate (CF_3CO_2^-), and heptafluorobutanoate ($\text{CF}_3(\text{CF}_2)_3\text{CO}_2^-$).⁷⁶

We have recently demonstrated that aromatic organic solutes partition to IL from water in relationship to their hydrophobicity as measured by their 1-octanol/water partition coefficients,²¹ and that reversible pH-dependant solvent extraction is possible.⁸⁰ Based upon these results, one would predict that hard metal cations would prefer the aqueous phase of a IL/aqueous system and the partitioning data obtained for metal cations between [Rmim][PF₆] and neutral, acidic, and basic aqueous phases thus far bear this out.⁸⁵ If metal ions are to be extracted from aqueous solution into the IL, extractants are needed in direct analogy to the use of extractants in traditional solvent extraction.

Utilization of Ionic Liquids in Biotechnology and the Generation of Renewable Feedstocks

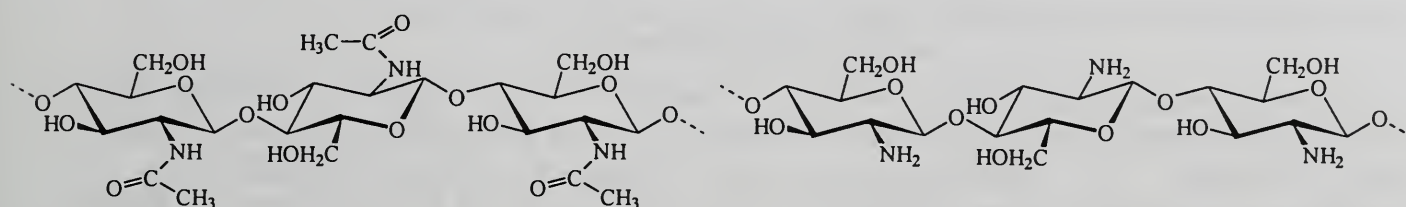
Chemical Feedstocks from Chitin and Cellulose. A major tenet in the Green Chemistry & Engineering paradigm is that a raw material or feedstock should be renewable, rather than depleting, wherever technically and economically practical.¹ However, both the chemical industry's *Vision 2020*² and the agricultural industry's *Technology Roadmap for Plant/Crop-Based Renewable Resources 2020*,³ stress the importance of lowering production costs and improving quality of such raw materials. Key goals and opportunities in these areas include new separations technologies to better handle heterogeneous plant components and advanced (bio)catalysts for monomeric and polymeric conversions. Interestingly, these same opportunities were listed as key barriers standing in the way of developing a Carbohydrate rather than Petrochemical economy.

Preliminary (unpublished) results in CGM laboratories have demonstrated that two major sources of carbohydrates, cellulose and chitin, can be directly dissolved in [C₄mim][Cl],⁸⁶ and that the IL may serve as the solvent for further chemical modification of these pyranose-based moieties. In addition, a single report in the literature has shown that effective enzymatic transformation can indeed occur within an IL matrix.⁸⁷ These results are exciting and suggest that a viable research program in the dissolution and chemical modification of plant-based materials is possible.

Solubilization and Modification of Cellulose. Cellulose has proved in the past an intractable material in industrial use. The multiply hydrogen bonded nature of this naturally occurring polymer has prevented its wide use as a source of chemical feedstock or its development as a technologically advanced material despite its being the most abundant of the natural polymers. Typical procedures for its isolation and fractionation involve high temperatures and demanding solution conditions.⁸⁸ Examples are the conditions of the Kraft pulping process, with its high levels of alkali and high temperatures resulting in poor yields. Other examples include the use of high concentrations of chaotropic salts such as calcium thiocyanate, or of solvents doped with LiCl. Such processes use large amounts of chemicals and energy and are unlikely to be viable for the production of chemical feedstocks to replace the current reliance on hydrocarbons.

Preliminary results in increasing the solubility of sugars in IL and in dissolving cellulose fibers in $[C_4mim][Cl]$,⁸⁶ make it seem likely that the solvation properties of IL can be precisely tailored to provide dissolution at ambient temperatures of a wide range of natural carbohydrate polymers. A wide range of derivatization and catabolic processes may be applicable in this environment and fractionation of products will be a key to success.

Solubilization and Modification of Chitin. Chitin (below, left) is a waste product of the seafood industry with an annual worldwide production estimated at 1.2×10^5 metric tons with total sales of chitin/chitosan expected to reach \$2 billion by the year 2000.⁸⁹ Chitin is a water insoluble cellulose-like biopolymer having several unusual properties that include toughness, bioactivity, and biodegradability.⁹⁰ The ability to solubilize chitin without degrading it would provide a useful avenue for processing chitin to its more versatile⁸⁹⁻⁹³ and water soluble derivative, chitosan (below, right).



Preliminary results in CGM laboratories indicate that chitin will dissolve in suitably chosen IL.⁸⁶ Thus far, the solubilities have been low, and a number of new IL need to be investigated, based on their water immiscibility, aqueous stability, and liquid temperature range.

SUMMARY AND CONCLUSIONS

Green Chemistry works towards reducing the hazard and environmental risk by designing chemical products and processes that reduce or eliminate the use and generation of hazardous substances. This novel approach to chemistry requires a fundamental shift in the current view of design and synthesis. Green Technology is R&D of new products and processes that are environmentally benign. Traditionally, synthetic chemists have not played a major role in the solving the environmental problems; that role has been left to analytical, physical, and atmospheric chemists. With the focus on designing new synthetic and analytical methods, all aspects of chemistry can be used to solve major environmental problems. By incorporating the twelve principles of Green Chemistry, industries can produce cost effective, environmentally-safe products.

The agriculture industry can play a major role in the development of green technologies. Plant/crop-based renewable resources are already being developed as alternatives to the fossil fuel-based materials the chemical industry currently relies on as feedstocks. The interrelation between these industries can be seen in both the engineering and processing of basic building blocks and in the manufacturing of consumer goods and recyclable materials. There has been, and should continue to be, a steady increase in the contribution to the economy by the agriculture industry, as well as an increase in carbohydrate-based materials used in the chemical industry.

The Clinton Administration (U.S.) and the U.S. National Research Council have developed a series of goals aimed toward the creation of a biobased economy.⁹⁴ The NRC predicts a nearly

complete conversion to biobased feedstocks by 2090 and President Clinton used an executive order to encourage tripling of U.S. use of biobased materials and energy by 2010. These actions confirm the importance of the agriculture industry to not only food production, but to providing raw materials that most other industries will need to survive.

Besides engaging in proactive R&D to meet energy market demands for renewable raw materials and feedstocks, the sugar industry can meet its current needs by looking at its own processing and production methods, and finding ways to maintain or increase yields while cutting waste production, handling, and disposal. The industry can grow new resources quickly and should provide alternative, environmentally benign materials that the petrochemical industry will continually find more difficult to provide. By incorporating the 12 principles of Green Chemistry, the sugar industry can provide not only its major food product, but also better materials and consumer goods that are more environmentally friendly and cost effective.

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HIGHLIGHTS OF TWENTIETH CENTURY PROGRESS IN SUGAR TECHNOLOGY AND THE PROSPECTS FOR THE 21ST CENTURY

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Introduction

Before dealing with the important technical progress in sugar processing during the finishing century, it is of relevance to glance at the preceding centuries to know where this industry comes from. Innovations in sugar cane technology were imposed by economic constraints in the 18th and 19th century. Labour and energy costs are two of the expenses to reduce if it is desired to increase profitability. As long as slavery was not abolished, there was no need for innovation. A technological advance and important economy of fuel was achieved by the substitution of firewood by bagasse and the introduction of the three-roller mill which leaves the cane stalks intact and combustible after drying. The second achievement was the Jamaican train, which consists of a battery of 5 or 6 cauldrons heated by one fire through internal flues, which improves the efficiency in fuel consumption. The battery is designed so that greater heat could be applied to smaller cauldrons than to the larger ones. The juice was clarified in the two first cauldrons and boiled to the point of crystallisation in the remaining cauldrons. Adding of rye, lime or ash was made by slaves who had to agitate, mix, skim or discharge a cauldron in another at temperatures above 100°C in conditions so bad as to be compared by a Jesuit Portuguese priest to a vision of souls in Hell.

Slavery was abolished in 1833 in English colonies and in 1848 in the French colonies. Heavy taxes were imposed on the importation of refined sugars in the metropolises. This was at the origin of the creation of refineries in England first, then in France. After slaves brought from Africa, there was an episode of transportation of cheap workers from China to the Caribbean Islands and South America.

The other historically remarkable fact was England's blockade of Europe after the Napoleonic wars, which led to the interruption of supply to the continental states. This was the trigger event for the sugar beet industry. Very rapidly and also because of the taxation policy, the sugar beet industry was developed. In less than a century (1850-1915) beet sugar production increased for 150,000 tons/year to nearly 8 millions of tons/year. The % of cane at the end of the

19th century was below 40% of the total sugar production. However, recovery followed in the early years of the 20th century. The First World War was fought in the fields of sugar beet and this contributed to the increase of cane share in world sugar production. It reached in 1919 a percentage of 78% not surpassed since that time (Galloway, 1989).

The competition between cane and beet sugar was one of the movers of the technology of sugar processing. Now, at the end of the twentieth century, owing to the emancipation of emerging economies, especially Brazil, and to the market laws, cane sugar is again at the rank with a production exceeding 73% of total.

It is beyond the scope of this presentation to analyse the economic and geopolitical reasons of the evolution of sugar production. We will keep within the limits of sugar science and technology. Alternately, mechanical engineering and chemistry were the two major disciplines governing the progress in sugar processing. We will recall the highlights of twentieth century innovations in sugar processing before presenting some of the perspectives we foresee for the twenty-first century.

1 – Evolution of sugar processing in the twentieth century

The basics of sugar processing were developed since the end of the 19th century, especially thanks to the numerous chemists of that period (Claasen, Hertzfeld, Grut, Stanek, Saillard, Wohryzeck,...). An indication of the importance of the progress in beet sugar processing in France may be derived from the increase in capacity of the factories. Whereas 300 factories having an average capacity of 200 to 250 tons/day were in operation around 1900-1905, to produce less than 1 million tons of sugar, only 40 factories continue to exist with a tonnage of 8000 to 20,000 t/day and a production of 5 millions t/year. Just after 1914-1918 world war, reconstruction of destroyed factories was made with a substantial increase in capacity with, in certain cases, central factories having satellite extraction units to solve the problems of conveying sugar beets to the factory. After the Second World War, the scarcity and cost of labour led to set continuous processes and to generalise the automatic control.

That was the period of intensification of basic and applied research. C.I.T.S (Commission Internationale Technique de Sucrerie) was launched in 1949. Setting of pilot workshops like that of G.T.S. (Groupement Technique de Sucreries) in France was established. The conception of equipment was modified for better efficiency, more and more continuous processes and centralised computerised control. Even sampling and laboratory analyses are more and more automated.

1.1. Extraction

Progress in plant breeding has been made since the last decades of the nineteenth century. It allowed an increase in % of sugar in beet from 8.8 to 18.8% in the period 1838 - 1908. The last years of the century are devoted to the controversial gene modification studies. Prediction of the technological value of sugar beet was proposed by Wieninger and Kubadinov (1971) using a formula for juice purity and molasses sugar based on the knowledge of the concentration of melassigenic non-sugars, Na^+ , K^+ and α -nitrogen, R being the sugar content of beet.

Juice purity :

$$P = 99.36 - 0.1427 \times (K + Na + \alpha N) \times 100/R$$

Sugar in molasses (as a function of alcalinity coefficient K_a)

$$K_a = (Na + K)/\alpha N$$

For $K_a > 1.8$: $S_m = 0.3492 \cdot (K + Na)$

$$K_a \leq 1.8 ; S_m = 0.6285 \cdot \alpha N$$

The coefficients of these equations are adapted to each crop of sugar beet depending on the composition of non-sugars.

Evaluation of sugar cane quality as concerns the quantity of sugar (pol) to be recovered was made since 1888 in Indonesia. Among the formula still used, the Winter formula gives the recoverable commercial sugar (W_s) as a function of pol (S_j) and Brix (B) :

$$W_s = S - 0.4 (B-S)$$

Of course the formulas used do not represent absolute values of sugar extracted and differ from one country to another. Although it is difficult to have representative sample of cane, Hugot (1974) recommends the direct analysis of a small sample after extraction of juice in a laboratory 3-roller mill or hydraulic press. The recoverable sugar (R.S.) is calculated using the formula :

$$RS = k \cdot (1 - 1.45 \cdot f) \times (S - 0.3 \cdot B)$$

Where k is an efficiency coefficient and f : fibre content, S sugar content in primary juice and B : Dry substance of primary juice.

Extraction of sugar evolved from batch maceration of beet gratings to methodical counter-current diffusion. Gain of time and efficiency were achieved together with the removal of polluting wastewater and the recycling of process water.

Batch vessels diffusion was commonly used in beet sugar factories during the first half of the century. In text books of the beginning of the century, one can realise how important was the labour cost. For instance, a sugar factory crushing 200 t/day needs for the batch diffuser :

- 1 batch operator
- 1 young assistant
- 2 workers for the cosettes (tamping down after vessel filling (with feet))
- 1 unskilled worker to sweep up
- 1 young assistant for different tasks.

Optimisation of sugar extraction by diffusion has been studied since the 1930's. The well known formula of Silin (1937) has only slightly changed during the following decades.

$$N(n-1) \cdot \log(n-1 + C/Co) / (n \cdot C/Co) = \gamma = A \cdot L \cdot Z \cdot \theta.$$

Where A = constant ; L = length of cossette % (m) ; Z = duration of diffusion (min.) ; θ = temperature coefficient ; γ = constant called “temporary constant” ; C = sugar loss in pulp ; C_0 = sugar content of beet (%) ; S = draft (L of juice % kg beet) ; $n = 0.93 (S + 0.43C_0)$. Labour costs and the advance of technology were at the origin of the numerous achievements of continuous diffusers. Many problems appeared in the early apparatus. These problems were either mechanical, due to the continuity of functioning or chemical, such as corrosion, foaming, bacterial growth and fermentation.

Very rapidly the advantages of continuous diffusers were indisputable :

- automatic control of operation
- optimisation of extraction.
- reduction of labour to a simple supervision form the centralised post of control
- increase in capacity of diffusers
- energy saving (by heat exchange raw juice/cossettes and juice/hot water).
- Recycling of press water with fresh water

Different types of a beet extractors are found in the end of this century based on different principles (Van der Poel et al., 1998) :

- controlled transport of both juice and cossettes (RT extractor, De Smet extractor)
- controlled transport of cossettes and uncontrolled transport of juice (silver chain-type, Olier)
- uncontrolled transport of juice and cossettes : towers extractors (BMA, Buckau Wolf), sloping trough extractors (DDS, silver slope-type).

Extraction of sugar from cane still uses crushing in a series of roller mills. A counter flow washing is applied. The whole milling process is completed after 20 minutes. Improvements were made at the level of the feeding of mills as is the case for the six-roll mill in Australia. Extraction is made more efficient as a reabsorption factor increases with roll surface speed. The quality of feed bagasse, the temperature and concentration of imbibition liquid may affect the imbibition coefficient, which is also sensitive to imbibition level.

Beside the classical cane mill, continuous counter-current diffusers were also used for cane sugar since the 1960's. Differences mainly related to the preparation of raw material exist between beet and cane extraction by diffusion. Adequate preparation of cane is needed to meet the requirements of efficient extraction in a cane diffuser. Different types of diffusers exist, most of them being inspired from beet diffusion, and generally constructed by the same suppliers as sugar beet diffusers (DDS, BMA, De Smet).

1.2. Juice purification

In sugar beet factories, the use of lime and carbon dioxide has been applied since 1859 according to a procedure set by the French Chemists Perrier and Possoz. At the beginning of the twentieth century, a massive liming (2-2.5 kg of lime % L of juice) was applied as well as double carbonation. Most of operations (filling, emptying, heating,...) were done manually. The

second half of century was that of modern factories inspired from achievements in cane sugar processing made in the U.S.A. The Benning carbonation saturator with external recycling of juice received simultaneously preheated raw juice and lime milk, which limits the alkaline degradation of hexoses and improves decantation and filterability. Static decanters (Dorr-Oliver) allow a good clarification. Clarified juice is fed into the second saturator where an excess of free CaO is removed and the sludge is filtered on continuous vacuum-drum filters. The main adjustments in beet juice purification are :

- progressive preliming of raw juice which allows a protection of the precipitate against desaggregation during massive liming
- a complete destruction of hexoses (low concentration in beet juice) during the contact at high pH in liming tanks prevents the risk of non enzymic browning reactions with the relatively high concentrations of amino-acids
- recycling of thickened sludge in the prelimer.

The important innovations in the field of juice purification which aimed at a better efficiency are :

- regular running of the whole purification chain owing to automatic control
- optimisation of thin juice quality because of a precise determination of pH, temperature and alkalinity optima (at the laboratory-pilot scale)
- centralised computerised control and labour reduction
- reduction in maintenance cost.

Meanwhile, an important increase in equipment capacity was achieved which reduces purification costs. The prevalent purification scheme corresponds to a pre-liming reaching an alkalinity of 2.8 to 3g/L. However, total lime used is below 15g/L because of recycling of first carbonation sludge in the pre-limer. So that the consumption of limestone remains around 19 to 25 kg per ton of sugar beet depending on draft (Bonnenfant, 1999). Consumption of lime has been decreasing regularly these last decades because of the improvement in the quality of beet and to technological advances.

In cane sugar manufacture, the juice purification used for several centuries is the simple defecation method (Honig, 1953). It consists of adding a small amount of milk lime to reach a pH close to 7.0 at a temperature of about 103°C before adding a flocculating agent to improve clarification. The clarifier underflow is mixed with bagacillo (fine bagasse) and desweetened on rotary drum filters. This original procedure was diversely modified changing the sequences of liming, heating and addition of phosphates or flocculants before clarifying.

The procedure of lime-carbon dioxide treatment applied for beet was also used to clarify cane juices. Lime consumption is lower than for beet, and the consumption of energy in a double carbonation purification system is higher than in simple defecation (Van der Poel et al., 1998).

Other innovations used in juice purification are based on the use of ion exchange resins. These are applied to decalcification, decolourisation or the exchange of Mg^{2+} ion, less

melassigenic against Na^+ and K^+ which are melassigenic. These techniques have drawbacks, as they produce large quantities of wastewater.

1.3. Juice evaporation

Equipment and processing are common in beet and cane sugar factories. At the beginning of 20th century, the basic principles were known:

- multiple – effect evaporation
- supply of vapour to the process
- vapour thermocompression

Important progress was made during this century:

- Thorough study of thermal scheme of sugar factories for heat economy achievement.
- Improvement of evaporators and heat exchangers (falling film, 2-body evaporator...)
- Increase in number of effects (2 to 3 in the beginning, now: six to seven effects with higher temperature of inlet steam and last effect under vacuum).
- Increase in efficiency by use of vapour compression (mainly in beet factory).
- rationalisation of thermal scheme including condensed water and other heat flows
- Because of sensitivity of cane juice to heat, reduction of time in first evaporator, limitation of boiling temperature or pressure, vacuum evaporation with elimination of condenser loss.
- Compliance with emission regulations in steam boilers (SO_x , NO_x , HCl , HF , CO , fly ash, soot).
- Better knowledge of the reasons for colour formation (sucrose hydrolysis, thermal degradation, retention times, omission of SO_2 addition for technical or regulation reasons).
- Scale removal by chemical cleaning or processing aids (polyelectrolytes).
- Concentration of thick juice for storage or crystallisation feed purposes (time saving during the footing of the crystalliser, decrease in vapour consumption).
- Advanced automation with computerised systems: better accuracy of measurement, supervision of plant from centralised control rooms, reduction of manpower, increase in safety.

1.4. Crystallisation

At the start of 20th century, solubility tables, boiling point elevation as a function of concentration and other physical chemical properties of sucrose solutions were known. However, the extraction of pure crystals from technical sugar solutions was a specialisation of the hand-picked personnel. The art of the pan man is to appreciate supersaturation and to grow crystals without formation of fines.

During the 20th century, the major improvements were :

- a better knowledge of sucrose solubility in water and of the properties of saturated solutions
- a systematic study of crystal growth rate as a function of supersaturation, purity and temperature
- a better knowledge of the effect of impurities on crystal growth and morphology
- studies were made of the molecular structure of saturated solutions and on the kinetics of nucleation
- in beet sugar factories, solubility in impure solutions is determined with a satisfactory accuracy using the variation of saturation (or solubility) coefficient as a function of non-sugar/water ratio (independent of temperature)
- in cane sugar factories, the high amount of invert sugar and mineral ions makes it difficult to predict the solubility coefficient

This is achieved at the laboratory using a saturoscope device. Such a determination of saturation point allows an approximate calibration of control devices.

- Continuous evaporating crystallisation was invented with advantages like constant flow, lower temperature between heating steam and magma, easier process control and the lower cost of investment and operation and disadvantages like a large C.V. of crystals, incrustations and the need to produce seeds outside the crystalliser.

Despite the advent of continuous vertical vacuum pans with improvements such as lower energy consumption, higher crystal yield, better process control (Kraus and Kordel, 1997), batch vacuum pans still are preferred in the factories because of an optimised commercial quality of sugar (grain size distribution and C.V., especially). Among the recent advances in crystallisation, we can give as an example, the mastering of the delicate process of seeding. This is based the theoretical principle of introducing the same number of particles as desired to find at the end of boiling after growth of crystals. Different seeding methods were developed recently. Seed magma was introduced into the CSM beet factory in Breda (Van der Poel, 1982) and further improved and computerised (Van der Poel et al., 1985). Another procedure was developed at the Braunschweig Institute with BMA (Eichhorn, 1991).

The operation consists in seeding a saturated syrup at high temperature with a slurry (10 μm of average size). Cooling crystallisation contributes to the growth of these particles. The magma obtained is used as a footing in a crystalliser where it should meet the requirements of uniformity of size and absence of conglomerates. Seed magma is needed for continuous vacuum pans.

Another interesting progress is that of the low product exhaustion. Owing to a better appreciation of parameters to optimise, especially as concerns the satisfactory work of low product centrifugals, it was possible to define precise set points for saturation and viscosity of mother liquor and compacity along the chain of low-product crystallisers. This was achieved using a pre-centrifugation step to reduce crystal percentage at the optimal value. Equipment at

this stage was also tremendously improved owing to the replacement of classical multiple crystalliser chain with large capacity vertical vacuum crystallisers.

1.5. Automatic control

The nineteenth century ended with the vanishing of old-style mills and the advent of central factories in most cane-growing regions. Only large factories could afford the sophisticated machines and the control instrument associated as well as the employment of qualified engineering staff.

One of the areas that is the most critical to run automatically was that of crystallisation. Different properties were used as variables in control loops for the automatic control of pan boiling. It is the case for electrical conductivity, as a reference for the supersaturation, which was adopted since 1932 in Java (Honig, 1959). Other variables like boiling-point elevation, refractometric Brix of mother liquor, viscosity, crystal content, level and temperature of massecuite, steam consumption or flow of syrup intake (Knovl et Moller, 1975/76) were applied.

Pneumatic and electro-pneumatic controllers were used. Generally, the tricky phase of filling, concentration, seeding, graining and thinning under low vacuum were controlled manually. The role of the pan man was preponderant.

Final boiling and tightening of massecuite was programmed. A considerable extension of automatic control to the whole crystallisation process was achieved in the 1960's. Increase in automation of the different steps of the sugar industry, together with the difficulty of finding highly qualified workers led to the construction of central control rooms with a few staff members able to control all process sections. In general, there were two control rooms, one for the head of the factory and one for the back.

Since the advent of computers and microprocessors, digital direct control was introduced with increased efficiency. The programmable logical controller (PLC) gave a better flexibility as the process control engineer is led to program a solution to the problems posed in the factory. Digital control systems where computers are connected by a bus prove to be the most reliable and robust tools of automatic control. The work in control rooms is now becoming one of the most important aspects in factory management (van der Poel *et al.*, 1998).

2 – Perspectives for the 21st century

The starting point of technological advances is always associated with a better knowledge at the molecular level of processes. This is also the case for sugar technology. Current progress and the perspectives of evolution of sugar processing originate from the rapid evolution of separation techniques first set for analytical purposes, then expanded at the level of pilots and factories. Likewise, structural and molecular studies of sugar, non-sugar and their interactions contribute to unveil some of the complex reactions occurring during the process.

2.1. New trends in analytical techniques

- Chromatographic methods:

Specific separation of sugars, anions and cations using highly selective ion exchange columns made the use of liquid chromatography more popular these last 15 years in sugar factories and research centres. This is due to the increase of sensitivity of pulsed electrochemical detection without derivatisation. It was possible using HPAEC-PAD to detect low levels (nanogram) of sugars, to identify polysaccharides after analysis of hydrolysates and to analyse minor constituents (organic and inorganic) of white sugar with a good accuracy.

- Infrared spectroscopy

Near infrared (NIR) spectroscopic methods have been developed as rapid, non-destructive, on-line tools for the monitoring of sugar processing. The method remains a secondary method depending on the calibration technique. This method has taken advantage of the recent advance in statistical methods (PLS, PCR), the development of fibre optics and the use of Fourier transform, which makes it of higher relevance than the black-box instrument when NIR came out.

Mid-infrared (MIR) also proves to be a powerful technique both for laboratory analysis and process control. The compact, robust, sealed new instruments may have a bright future in sugar factories owing to the wealth of information of the FTIR spectrum and the numerous accessories.

- On-line colour measurement:

A new system for on-line colour measurement was developed recently. It allows rapid measurements [less than 5 seconds], with no sample preparation. The fast feedback permits optimisation of washing time at the centrifugals and prevention of bad sugar entering the dryer. Uniformity and improvement of quality are reached with the use of the Colour Q-800 Neltec device. This method was tried successfully for white sugars to meet customer specifications. It seems also applicable to raw sugars entering in refinery for continuous analysis and monitoring of affination.

2.2. Membrane technology

The membrane filtration (micro-ultra- and nanofiltration) processes have been investigated in the field of sugar technology at different stages of fabrication, but mostly at the pilot-level. The feasibility of earlier generations of polymeric membranes was questionable as concerns the resistance of membrane to temperature, pH and damage by solid suspensions. Recent development of mineral membranes has allowed an increase in potential use of industrial ultrafiltration for cane juice purification (Cartier et al., 1996). The nanofiltration process has also been found efficient in the separation of salts and colorants from decolourizing resins elution flow. Coupling nanofiltration with decolourization resins was successfully used at an industrial level in cane sugar refineries (Theoleyre et al., 1999).

Cross-flow microfiltration was investigated as concerns the effect of monitoring conditions on performances when used for cane raw sugar remelts. Optimal conditions were defined and the role of optimal flux density emphasised (Trichard et al., 1998). A better

knowledge of the nature, structure and properties of retentate will improve the exploitation of membranes and lead the numerous pilot studies to industrial applications.

- Chromatographic separation

The chromatographic separation of molasses has been used for desugarization of beet molasses since the 1970's. High levels of calcium and magnesium salts in cane molasses make it difficult to apply chromatographic separation. The possible use of chromatography for low green and thick juices was recently discussed (Paananen, 2000). The improvement of technology and the economic aspects of replacing classical technology of boiling, remelting and boiling again by a process including chromatographic separation does not seem irrelevant.

Simulated Moving Bed (SMB) chromatography has been applied to the desugarization of both beet and cane molasses. The SMB-process was developed as a continuous system where counter-current flows of resin on the one hand and molasses on the other were changed at regular intervals to meet balanced rates at the inlet and outlet. Improved Simulated Moving Bed (ISMB) brings further advantage like the reduction of resins volumes, the optimisation of water elution quantities and a minimisation of the dilution of purified product, which gives energy saving in evaporation.

2.3. Combining innovating technologies and the perspectives for the 21st century

No single technology can solve both economic and process constraints. The future of sugar technology relies on a near-real time adaptation of the sugar processing to solve technical problems, comply with regulations (safety, environment, quality assurance) and in the meantime increase profitability. The future sugar factory will not use a common layout for all types of crops, climates and sociological conditions of workers.

There should be three types of approaches. The beet sugar factory in North Europe and North America where environmental constraints, together with highly qualified manpower and the possibility of higher investments can allow a high-tech sugar processing (Type 1).

The cane sugar factory in the important regions of cane production (Australia, South Africa, North and South America) while using the same technologies as beet should think of optimising the inversion of sucrose and move towards the production of multicomponent sugar syrups. Why not a HFCS (where C would mean cane)? This is not senseless as we see how reluctant the consumer is to accept corn syrups from transgenic crops (Type 2).

Finally, for developing countries, small workshops would be better adapted to the local economy and sociology of workers. Small scale factories using modern concepts and standards should be economically viable (Type 3).

2.3.1. Combining membrane separation ion exchange and cooling crystallisation in beet sugar factories (Type 1).

The recent extensive research on the possibility of crystallising raw juice directly by use of cooling crystallisation (Vaccari and Mantovani, 1987) showed the advantages of this method over classical evaporation crystallisation. Combining cooling crystallisation with microfiltration (Mantovani and Vaccari, 1998) was found to be efficient for obtaining white

sugar directly from the first strike together with good exhaustion of molasses. These experiments at the level of the laboratory and the pilot plant were also tried for cane sugar raw juice for which the classical calco-carbonic purification was replaced by microfiltration and simulated moving bed chromatography (Mantovani and Vaccari, 1999). Raw sugar refining can also use cooling crystallisation after decolourizing the affinated syrup and filtration instead of the classical phosphatation or carbonation. Moreover, working at low temperature favours the concentration of fructo-oligosaccharides (kestoses) in cooling crystallisation molasses. The use of ISMB can help recovery of betaine on the one hand, fructo-oligosaccharides and sucrose on the other. The added value of betaine in feed and cosmetic applications and the use of kestoses as prebiotic nutrients can help improve the profitability of the new process.

Flow diagrams of the cooling crystallisation of raw beet juice were proposed by Mantovani and Vaccari (1999). The main advantages in this new processing are:

- elimination of calco-carbonic purification
- reduction of the consumption of fuel, limestone and water
- environmental protection by minimising waste

The addition of innovative technologies such as the evaporative process for recovery of dissolved solids in very dilute process streams (Ramm-Schmidt, 1996) to the microfiltration-cooling crystallisation scheme may help in eliminating all types of waste and recycling water. Application of the new evaporation technology was applied successfully to the chromatographic desugarization process by SMB chromatography. It was at the origin of energy saving, increase in capacity of plant, increase in purity of fractions and economical feasibility of recovery of new dilute fractions (Ramm-Schmidt, 1996).

2.3.2. Separation processes and enzymatic technologies applied to cane raw juice (Type 2):

Like beet juice, raw cane juice can be purified without having recourse to calco-carbonic methods. Different separation processes were proposed as an alternative to liming. It is the case for the "A.B.C." process, which consists of continuous screening, ultraclarification and adsorption of colorants (Monclin and Willett, 1996). The Amalgamated sugar company proposed a chromatographic separation process for raw beet or cane juice which replaces liming and carbonation efficiently (Kearny, 1996). Such a process allows direct production of white sugar in the mill. It can use either the classical evaporation crystallisation or the innovative cooling crystallisation method. Membranes are also efficient in the cane sugar factory. Ultrafiltration reached the removal of 90% of turbidity and 20% of colorants using Techsep mineral membranes for the treatment of cane raw juices (Cartier et al., 1996).

Membrane technology as well as SMB chromatographic separation are also well known in glucose syrup manufacture. Purified raw cane juice can be inverted using immobilised invertase and separated into fructose and glucose. Enzymes such as dextranases and amylases may be introduced during the extraction step to help recover the polymerised glucose. Direct production of sugar syrups with varied concentrations in D-glucose, D-fructose and sucrose to meet the demand of the food industry can come about out as a response to the reluctance of customers to use transgenic corn syrups. Diversification of the production of different crystalline

sugars grown in cooling crystallisers (α -D-glucose monohydrate and sucrose) and different formulas of glucose-fructose-sucrose syrups may prove to be a flexible solution to a continuously changing market.

3 – Small scale factories (type 3) :

The present trend to increase the capacity of sugar factories is reaching its maximum. Such a trend can suit for an expanding economy where labour cost is minimised together with an increase in high-tech equipment. For developing countries, sugar remains an important energy source in the diet. The situation of employment is such that mechanisation is not advised for all sectors of activity in sugar production. Process development should use batch processes with adapted automated control. The unit operations chosen for the sugar factory flow sheet in a developing country should not be a simple transfer of what the equipment suppliers recommend for European or North American industries. Crucial problems such as the lack of potable water, the need for job-sharing and eventually full employment have priority as compared to increases in yield and profitability. Utilisation of efficient extraction technology like the inverted 3-roll mill in which drainage takes place in the same direction as the bagasse flow (Sullivan, 1995) can be associated with flocculation and cross-filtration to remove impurities from raw cane sugar juices. These units of extraction and purification should have the right size to avoid costly transport of cane. Purified raw juice can be crystallised using either batch evaporation or cooling crystallisation pans for the home market. The developing countries can also comply with organic sugar regulations and specialise in this type of production for exportation. A minimum of international solidarity is needed if it is desired to reduce the huge gap between the economies of Northern and Southern countries.

Conclusion

The sugar industry is an old industry which is now reaching maturity. It has evolved with profitability as its predominant objective. It is now being competed with by both artificial sweeteners and glucose syrups. Because of the high level of the technologies invented or improved to optimise energy saving, environmental protection and quality assurance, it is again possible for the sugar industry to relaunch a rational market-share between the different producers of beet or cane. Technologies can be adapted to the specific countries. Awareness of the human dimension of such an activity as sugar production, which associates agriculture, engineering, processing, automation, and education for an adapted qualification should be born in the mind of decision-makers. The twenty-first century should combine modern technologies in Northern countries for increased profitability and help the developing countries in keeping a modernised industry protected from the tough law of the market.

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BIOTECHNOLOGY AND THE NORTH AMERICAN BEET SUGAR INDUSTRY

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Introduction

Food producers in North America rely heavily on the sugarbeet industry for their annual supply of sugar. In fact, the United States Department of Agriculture, Economic Research Service estimates that the 1999 sugarbeet crop will reach a record 1.5 million acres, yielding 34 million tons of beets and producing approximately 4.2 million tons of white sugar. (1) In 1999, Canada will harvest 44,300 acres, yielding 925,000 tons of beets and producing nearly 120,000 tons of white sugar.

Between the two countries, over 10,500 growers produce sugarbeets. In the United States, sugar beets are grown in eleven states, California, Colorado, Idaho, Michigan, Minnesota, Montana, Nebraska, North Dakota, Ohio, Oregon, Washington and Wyoming. Canada has production in two provinces, Alberta and Ontario.

However, sugarbeets are a challenging crop to produce. Sugarbeet cultivation is highly sensitive to insects, diseases and weed competition and requires continuous monitoring and management for control of these pests. Insects, diseases and weeds begin attacking the sugarbeet crop from the time of planting and continue through harvest. Other production difficulties include water management and control, temperature extremes, including heat and cold, and long term storage in some areas.

As a result, sugarbeet growers must work diligently to control these pests with hand labor, mechanical weed removal and pesticide applications. The industry continually looks for ways to enhance pest control and ultimately improve yields and sucrose content. Cultural practices, such as irrigation and tillage are also important tools. For more than 60 years, plant breeders have worked with genetic material of sugarbeets through conventional plant breeding, commonly referred to as hybridization, to provide the healthiest and most disease resistant plants possible. Modification of other traits, such as the shape of the root, have also been explored. The next step in the evolution is to improve pest control and crop quality through plant biotechnology. This paper will address the implications of plant biotechnology in the North American sugarbeet industry.

Background on Biotechnology

Biotechnology is the application of living organisms to develop new products. Although the term biotechnology has gained widespread recognition in recent years, the science has been with us for centuries. For example, in 1800 BC, with the use of fermentation, man first harnessed organisms to produce wine, beer and leavened bread.

Plant breeders have employed these same principles in crop hybridization for the past 60 years. Crop hybridization combines genes from a plant with desirable traits (such as increased yield or resistance to insects or diseases) with a commercial variety to produce an improved plant. For example, Rhizomania and Cercospora resistant varieties are hybrids developed to confer disease protection on sugarbeet plants.

Plant biotechnology isolates and transfers a single genetic trait from a plant or other organism, rather than crossing one plant's entire genetic material with another. This allows the transfer of a selected, desirable trait in a more controlled manner than with traditional plant breeding.

Genetically enhanced plant seed available today offers growers options to convert to no-till and low-till farming practices and to decrease their use of pesticides, reduce labor and allow more timely management of crop production. The plants grown from these seeds offer processors and consumers cleaner products with fewer complications caused by trash or foreign debris.

Other possibilities for plant biotechnology to improve crops include:

- Instilling built-in tolerance to a specific herbicide, thus affording growers more flexibility in timing herbicide treatments, choosing more desirable herbicides, or reducing overall herbicide use;
- Instilling built-in protection against a specific insect or plant disease that could cut yields or even destroy a crop;
- Building in vital additives to animal feed;
- Allowing improvements in processing efficiency;
- Improving nutritional value;
- Improving flavor.

In 1998 a broad range of genetically enhanced plants were made available to growers in a number of countries worldwide. Some of the companies commercializing these plants included AgrEvo, Betaseed, Calgene, Du Pont, Dow/Mycogen, Monsanto, Zeneca/Petoseed, Asgrow, and Novartis, to name a few. The following is a sample of the transgenic plants available:

- Herbicide-tolerant maize, canola, cotton and soybean
- Virus-resistant squash, tomato, tobacco and papaya
- Insect-protected potato, cotton and maize
- High oleic acid soybean
- Laurate canola
- Golden Rice

According to the International Service for the Acquisition of Agri-biotech Applications (ISAAA), between 1996 and 1998, eight countries contributed to a more than fifteen-fold

increase in the global acreage of genetically enhanced crops, resulting in a total of nearly 70 million acres. Growers in the United States, Argentina, Canada, Australia, Mexico, Spain, France and South Africa planted genetically enhanced seed, primarily soybeans, maize, cotton, canola and potato. The rank-order of the principal transgenic traits in the planted seed is: herbicide tolerance; insect-protection and quality traits. (14)

Once growers harvest and ship genetically enhanced commodity crops to food producers, the products of these crops are incorporated into scores of goods. For example, over one-third of the corn planted in the United States in 1999 was genetically enhanced. (15) After harvest, as in previous years, this corn will be processed with traditionally grown corn and will help meet the demands of products ranging from animal feed to corn syrup sweeteners.

In addition to grower satisfaction, genetically enhanced foods will help meet the growing global food demands. According to a 1998 report of the World Health Organization (WHO), the global population of about 5.8 billion will increase to about 8 billion by the year 2025. (16)

The accelerating world population taxes an already strained agricultural base. In order to produce enough food, farmers worldwide will need higher-yielding plants that require fewer inputs, like pesticides and fertilizers. Because plant biotechnology offers plants with beneficial traits not possible before, the science holds great hope for agriculture.

North American Regulatory Policies on Plant Biotechnology

Scientists worldwide are studying many ways they can develop plants that offer the advantages made possible through plant biotechnology. Although there often is collaboration and consensus within the scientific community, each country continues to operate its own regulatory systems that govern the development, planting and commercialization of genetically enhanced crops.

There are two types of herbicide-tolerant sugarbeet plants that have been reviewed or are being reviewed. The genetically enhanced sugarbeet tolerant to glyphosate (marketed under the name Roundup Ready®) has been reviewed and cleared by all three of the U.S. regulatory agencies: the Environmental Protection Agency (EPA), the Food and Drug Administration (FDA), and the U.S. Department of Agriculture (USDA). Roundup Ultra® has been registered for use over the top of Roundup Ready® sugarbeets by the EPA. These sugarbeets have been cleared after consultation with the FDA, and granted non-regulated status by the USDA. (10,11,12,13) The sugarbeet resistant to glufosinate (marketed under the name Liberty Link®) has been cleared by two of the three agencies, FDA and USDA; as of this writing, EPA registration of Liberty® herbicide for use on Liberty Link® sugarbeets is pending. Makers of both genetically enhanced sugarbeets are awaiting clearance from regulatory agencies in various world markets.

United States Regulatory System

U.S. Food and Drug Administration

The U.S. Food and Drug Administration (FDA) completed its review of the new sugarbeet plants with a built-in tolerance to specific herbicides and confirmed their food and feed safety. (12,13)

FDA is the primary agency responsible for ensuring the safety of food and feed products. FDA establishes guidelines to evaluate a new plant for “substantial equivalence” with the plant’s traditionally grown counterpart. “Substantial equivalence,” or “equivalence,” in this context means there is no meaningful change in the nutritional value or composition of the food. FDA does not require any special handling or labeling of the food and feed produced from genetically enhanced crops that are equivalent to traditional crops. Genetically enhanced crops are mixed, or co-mingled, with traditionally grown crops. Since 1996 the United States has harvested millions of acres of crops grown with genetically enhanced seed and processed these crops with their traditionally grown counterparts. The processed portions of such crops then are distributed and used in end products in the food and feed industries.

U.S. Department of Agriculture

In 1998, the Animal and Plant Health Inspection Service (APHIS) – a division of the U.S. Department of Agriculture (USDA) – completed its review of the new herbicide-tolerant sugarbeet plants, and confirmed their agricultural and environmental safety.(10,11) The USDA regulates agricultural products and research – including the development of new plants. APHIS’s role is to ensure that new plants pose no threat to production agriculture or the environment. APHIS regulates research development by requiring permits for field-testing, shipping and delivery of any seed or plants modified through biotechnology.

U.S. Environmental Protection Agency

In March 1999, the U.S. Environmental Protection Agency (EPA) completed its review of Roundup Ultra® herbicide for use over Roundup Ready® sugarbeet plants and registered the new use of this herbicide. (17) Use of Liberty® herbicide currently is being reviewed by EPA for use on Liberty Link® sugarbeets. EPA regulates any pesticide that may be present in food and sets tolerance levels to provide a high margin of safety for consumers. As part of this responsibility, EPA regulates new uses of herbicides, such as the use of a new or existing herbicide on a new plant that is tolerant to that specific herbicide.

Canadian Regulatory System

Canada’s regulatory system governing new plants is similar to that of the U.S., in many ways paralleling the three U.S. agencies. Health Canada oversees food safety in Canada. Agriculture and Agri-Food Canada regulate feed and environmental safety, as well as registration of specific plant varieties for certain crops. The Pesticide Management Regulatory Agency regulates pesticide use in Canada.

Roundup Ready® sugarbeets as novel food are in the review process and regulatory clearance is expected in early 2000. Roundup Ready® sugarbeets as novel feed were submitted in June 1999. Application for Liberty Link® sugarbeets as novel food was made in February 1999. Approval was expected by the end of 1999.

Application has been made to the Pesticide Management Regulatory Agency for registration of the use of Roundup® and Liberty® over the top of the respective transgenic sugarbeets.

Sugarbeets and the Implications of Biotechnology

Plant biotechnology is different from hybridization because it involves isolating and transferring a single gene trait from a plant or other organism – rather than crossing one plant's entire genetic makeup with another. Plants developed through this science have a number of beneficial traits. Some examples include disease protection, insect protection, herbicide tolerance to a specific herbicide, and improved food quality.

Plant biotechnology was recently introduced in commercial maize, potato, canola, cotton and soybean production. The resulting plants are called genetically enhanced, or transgenic. New sugarbeet plants are available that are genetically enhanced to tolerate specific herbicides, a trait that offers both economic and environmental benefits to growers and processors. The new plants allow growers more flexibility in timing their herbicide applications and the option to use fewer and/or more desirable herbicides. Fewer applications mean fewer trips across the field, resulting in less soil erosion and less compacting of the soil.

Sugarbeets are biennial and have a two-year life cycle. (2) In the major production areas sugarbeets are grown for only the first year of the life cycle. During this time they are in a non-reproductive stage and produce large storage roots that are harvested for sugar extraction. Generally, sugarbeets are not allowed to develop seed or cross-pollinate with other plants. This greatly reduces the chance of genetically improved sugarbeets transferring herbicide-resistant qualities to other plants or weeds.

Sugarbeet seed is generally planted in April or May and harvested in the fall. After growers harvest the crop, sugarbeet processors recover three products from the sugarbeet root: sucrose, molasses and beet pulp. The processor first extracts sugar from the beets, purifies the juice using lime and carbon dioxide, then crystallizes the sugar. The sucrose derived from these plants is highly processed and has the same chemical composition as sugar processed from conventional sugarbeets. (3) Both genetically enhanced and conventional sugarbeets are processed the same way.

During extraction, beets are washed, sliced and placed in a diffuser. The diffusion process exposes the beets to temperatures of approximately 72 degrees Centigrade (161°F) (4) and levels of sulfur dioxide in the range of 50 to 100 parts per million (5), or other micro biocide agents. The beet pulp is pressed and dried for cattle and other animal feeds. The conventional process exposes the pulp to temperatures of 650 to 1000 degrees Centigrade (1202 to 1832°F). It is dried for approximately 15 to 20 minutes. (6) The juice that is extracted in the diffusion process is heated and exposed to a liming process reaching temperatures of 95 degrees Centigrade (203°F) and pH values of 12 for approximately 20 minutes. (7) This process removes 20 to 35 percent of the impurities from the juice. The juice is then filtered, concentrated at temperatures of 120 to 135 degrees Centigrade (248 - 275°F), and sent through the crystallization process. (8) The juice is further concentrated to a density that supports the formation of crystals. The crystallized sugar (now 99.5 percent sucrose, the remainder being moisture and inorganic salts) is dried and sent to storage. (9) The extreme temperatures and the crystallization process ensure the purity of the final product, whether the sugar is from genetically enhanced sugarbeets or conventional sugarbeets. The portion of the juice that will not crystallize because it contains too many

impurities is molasses. Molasses is used for cattle feed, yeast manufacture and various other industrial applications.

The majority of sugar produced from U.S. sugarbeet crops is sold within the country for domestic use. Much of the sugarbeet pulp is exported to Japan and/or Europe. Molasses is sold primarily domestically, occasionally abroad.

Current Research Programs and Direction

Public

The Beet Sugar Development Foundation works cooperatively with the United States Department of Agriculture, Agriculture Research Service (USDA/ARS). Through our long standing Memorandum of Understanding, and by providing some funding, the sugarbeet industry in North America actively participates in the research direction at the USDA/ARS research stations across the country. There are currently six active ARS sugarbeet research stations in the United States. These are located at Salinas, California; Ft. Collins, Colorado; Fargo, North Dakota; East Lansing, Michigan, Urbana, Illinois and Beltsville, Maryland. Although they do work in many other areas of sugarbeet research, each of these research stations has a biotechnology component.

Salinas, CA

One segment of the Salinas laboratory of the USDA/ARS is involved with virology. In particular, the virus yellows complex that infects sugarbeet. The scientists working at this facility are using sugarbeet tissue culture technology in combination with plant transformation to develop pathogen-derived resistance (PDR) against viruses that infect sugarbeet. Pathogen-derived resistance involves the insertion of genes from a pathogen into the genetic material of a plant to provide resistance against that pathogen. Current efforts are underway to identify viral gene sequences that interfere with the ability of Closteroviruses such as beet yellows virus and lettuce chlorosis virus to infect sugarbeet. This project, on the development of Closterovirus resistance through biotechnology, is integrated into a complex research program to identify, understand and control viruses responsible for virus yellows of sugarbeet.

Ft. Collins, CO

The USDA/ARS Sugar Beet Research Unit at Ft. Collins is using biotechnology to better understand the sugarbeet-pathogen interaction and, thereby, help increase the speed and efficiency of crop improvement. They also are using molecular markers directly to provide more and better tools in the sugarbeet breeding effort. These markers differ in cost, ease of use, frequency in the plant, but all have been effectively used in crop improvement programs, genetic diversity studies, and gene bank management. Molecular markers are based on the plant DNA sequence and include Restriction Fragment Length Polymorphisms (RFLPs), Random Amplified Polymorphic DNA (RAPDs), Minisatellite DNA, and Simple Sequence Repeats of DNA (SSR) – also called microsatellite DNA. Molecular markers in sugar beet have been used in a number of ways to complement breeding efforts using material from the Plant Introduction (PI).

Fargo, ND

The program at the USDA/ARS station in Fargo is involved with biotechnological approaches aimed at solving sugarbeet disease problems. Naturally occurring genes in sugarbeet that confer resistance to pathogens are being tagged with DNA-based markers. This will facilitate breeding programs aimed at incorporating this resistance into hybrid parents, as well as lead to eventual cloning of such genes so that they might be improved upon. Gene transfer technology also is being applied to the sugarbeet fungal pathogens, *Cercospora beticola*, *Pythium ultimum*, *Aphanomyces cochlioides*, and *Rhizoctonia solani*. Application of this technology will yield greater insight into the biochemical arsenal used by these fungi to cause disease in sugarbeet plants. Knowledge gained by these studies will aid in the development of rational strategies for disease control either by use of transgenic sugarbeet or by application of antifungal agents.

East Lansing, MI

Biotechnology at the East Lansing USDA/ARS station encompasses a number of diverse, related activities geared towards understanding the genetic components of sugar accumulation, disease resistance and seedling emergence traits. Most, if not all, traits are controlled through an interaction between genes and the environment. The focus at East Lansing is to dissect these traits and locate their genes so that they can be used for sugarbeet improvement. There are a number of ways that this is being accomplished. These include generating segregating populations with different combinations of traits using either genetic self-fertility or haploid plants obtained via ovule culture, gene mapping using molecular markers, characterizing the beet genome, and analyses of gene expression.

Urbana, IL

The USDA/ARS laboratory located in Urbana, unlike the other USDA locations is not involved with pest control or resistance in sugarbeet. However, they are involved in the physiological aspects of sucrose production in the sugarbeet. They are investigating assimilate partitioning and sucrose transport. They have identified an essential amino acid residue in the sucrose transport protein that is responsible for the long distance transport of sucrose from the leaves to the taproot of sugarbeet. They have subsequently replaced that critical amino acid with other amino acids and have shown that some of these changes improved transport activity by ten-fold. They are using recombinant DNA techniques to introduce the modified transporter into sugarbeet taproot tissue to test the idea that its hyperactivity may lead to higher levels of sucrose accumulation.

Beltsville, MD

Basic transformation and regeneration of sugarbeet is the primary focus of the USDA/ARS group working at Beltsville. Sugarbeet is a difficult plant to transform and regenerate, unlike other crops, such as tobacco. The Beltsville laboratory is investigating various different transformation and regeneration techniques to increase the success of these processes. This research is vital to the continued future of biotechnology in sugarbeet. This group is also working on producing parental lines that exhibit resistance to *Cercospora* leaf spot, *Rhizoctonia* root rot and *Erwinia*, along with using inhibitor genes that specifically target digestive enzymes in the sugarbeet root maggot.

Private

Commercial sugarbeet seed companies are also actively involved in research and development in biotechnology in sugarbeet. These companies fully respect the concerns of consumers and food processors regarding genetically enhanced sugarbeet. However, with regards to farmers' interests, environmental needs and the necessity to dramatically increase productivity of land in the long run, they are fully committed to biotechnology as a means to serve these ends. They are actively involved in research and development regarding virus resistance, fungal resistance, nematode resistance and quality traits of sugarbeets. The technological developments made by the public sector researchers, mentioned above, will be available to the private sector to aid in these future developments.

Conclusions

In summary, as the sugarbeet industry moves into the next century, the introduction of desirable genetic traits through plant biotechnology holds great promise for the industry's continued growth and success. Herbicide-tolerant sugarbeets demonstrate significant agronomic advantages. This, however, is only the tip of the iceberg. The use of biotechnology for insect and disease resistance, along with the modification of the physiological function of the sugarbeet, whether it be to increase sucrose production or to produce other products are goals which are now actively being explored. Finally, consumers worldwide will continue to enjoy food products sweetened with sugar produced from sugarbeet.

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PROCESS DESIGN CRITERIA FOR A MODERN SUGAR REFINERY

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INTRODUCTION

As the cane sugar refining industry enters the 21st Century, it faces challenges from many directions. These include, to name but a few, environmental issues, oversupply of sugar and consequent low price obtained for products, increased competition from alternative sweeteners and producers in other countries, and constantly escalating labor costs.

For a modern refinery to meet the challenges of the 21st Century, certain design criteria must be met. The new refinery should be designed with six critical elements in mind. These critical elements deal with manning requirements; sucrose loss on raw sugar received; total energy consumption; specific raw sugar pol values in order to maximize efficiency; sucrose carried to molasses, and maintenance costs.

Numerous plant design requirements are needed in order to achieve the above critical elements, since there are over 25 points in the refining process where control points and critical limits must be specified for parameters such as temperature, pH, density, color, turbidity, conductivity, purity, and vacuum pressure. The use of on-line continuous testing instrumentation is an important aspect of efficient control. The recommended design criteria for each refinery process is herein discussed in some detail.

THE BASIC PRINCIPLES OF CANE SUGAR REFINING

There are 20 basic principles of cane sugar refining, which are shown in Appendix 1 (courtesy of C&H Sugar Co., California, USA). In essence, they resolve around a few simple ideas, which are not always easy to implement in practice. These are to (1) optimize separations; (2) keep stocks small, operate fast and clean, and minimize the number of processes, while having each unit process as large as economically feasible; (3) water control, such as minimizing evaporation; and (4) preserve the integrity of the product once it is made by avoiding rework or redissolution of crystallized material. To these can also be added the necessity to minimize recycling of impurities throughout the process.

THE GOALS

To meet the challenges of the 21st century, a new refinery should be designed with the following goals in place:

(1) **Manning.** No more than four operators per shift from raw sugar receipt to sugar conditioning, screening, including boiler operation, electricity generation and waste water treatment. However, operation for packaging of sugar is not included in this figure because the number of packaging operations depend greatly on the company's product mix. Simplification of refinery processes is also required in order to achieve the goal.

(2) **Sucrose Loss.** A sucrose loss of no more than 0.55% on raw sugar received. Sucrose loss is defined as sucrose in raw sugar less sucrose in product shipped and sucrose carried to blackstrap molasses. Packaging overfill is also included in the sucrose loss. A 0.2% of excess sucrose loss would cost a company with a refining capacity of 1,200 tons/day operating 330 days/year as much as US \$350,000 at \$440/ton of raw sugar in the U.S. sugar market.

(3) **Energy Usage.** A total energy usage of 70 liters of No. 6 oil per ton of raw sugar processed operating 250 days/year with weekly shut-down. This is equivalent to 3136 megaJoule/ton or 134.85 MBTU/cwt or 2,973 MBTU/ton of sugar. For a refinery running continuously for 340 days/year, the total energy consumption should be significantly less than 60 liters/ton. In fact, there is no reason that steam consumption should exceed 0.5 ton of steam per ton of raw sugar processed, if the plant is properly designed and operated.

(4) **Raw Sugar Quality.** For optimum process efficiency, raw sugar polarization should average more than 98.3. Attempts should be made to avoid purchasing raw sugar with less than 98.0 pol.

(5) **Sucrose to Molasses.** Sucrose carried to blackstrap molasses should not exceed 0.8% of sucrose in raw sugar processed. To achieve this goal, the blackstrap molasses purity should be less than 45; non-sucrose content eliminated by the refining process should be at least 10%, and some low purity products should be incorporated in the over-all product mix.

(6). **Maintenance Costs.** To achieve minimum costs, instrument and equipment selected needs to be reliable as well as precise and accurate. Refining processes and unit operations need to be simplified. The maintenance costs (including labor) should not exceed 20% of the total cost of production.

PLANT DESIGN REQUIREMENTS

The following sections enumerate plant design requirements which would be needed in order to achieve the above mentioned goals.

1. pH Control

Without proper pH control and technical set points established at various stages of the process, it would not be unusual to experience a sucrose loss of over 1.0 percent of raw sugar melted. The magnitude is substantial; an increase of 0.5% sucrose loss (i.e., from 0.5% to 1.0%) would cost a refinery with 400,000 tons/year capacity approximately U.S. \$880,000 per year at a raw sugar price of \$ 440 per ton in the U.S. market.

2. On Line Continuous Testing Instruments

In addition to temperature and density controls at various points in the refining operation, the following are essential to maintaining process and operating efficiency. All listed instruments below are commercially available:

- A. Colorimeters for remelt liquor, melt liquor, press filtered liquor and fine liquor to the pans.
- B. Turbidity meters for press filtered liquor.
- C. Purity analyzers for remelt liquor, and affination syrup.
- D. Sugar detectors with minimal use of hazardous chemicals and waste generation should be acquired for both condenser water and sewer discharge.
- E. Continuous on-line moisture analyzer of granulated sugar products.
- F. Continuous on-line color measurement of granulated products.

3. Process Control and Specifications

There are over 25 points in the refining process for control of temperature, pH, density, color, turbidity, conductivity, purity, and vacuum pressure, etc. The control points and critical limits for each unit operation or process must be specified. This ensures that the refinery will perform at top effectiveness at optimum conditions, and produce consistent high quality product minimizing the need for laboratory testing.

A dynamic matrix controller (DMC) employed in a popular distributed control system (DCS) should be sufficient to limit manning to only five operators per shift or less between the raw sugar warehouse to sugar drying and storage. The essential point to remember is that the key to the success of any control system is based on sensing and measuring devices. Therefore, it is of utmost importance to carefully evaluate and select the sensing and/or measuring devices.

4. Energy Usage and Water Consumption

Presently, the total energy usage of a "best" run refinery with a carbonation facility is about 3,200 megaJoule (MJ) per ton of raw sugar processed. The level of 75 liters of No. 6 oil is equivalent

to 3,500 MJ per ton of raw sugar processed. The average total energy usage in the sugar refining industry is about 4,200 MJ/ ton of raw sugar with weekly shut-down.

The total refinery water usage, excluding water for the condensers, of a "best" run refinery is about 200% of the weight of raw sugar melted. An average refinery probably runs at 285% of raw sugar melted. The more water that is used, the higher the energy required for evaporation and the higher the sucrose loss, resulting in poor sugar yield. The keys to minimizing energy usage and water consumption are prudent process selections and a good U. C. (utility conservation) program. A heat train to recycle energy resources should be an integral part of the turn-key design system. All the vapor should be re-used whenever possible to the limit of the second law of thermodynamics. For reasonable process efficiency, the polarization for raw sugar process should not be less than 98.3.

5. Process Selection and Design

A. Raw Sugar Warehouse

For versatility in handling different raw sugars, a tunnel conveyor spanning the full length of the warehouse with at least 30 floor openings should be built. Raw sugars of various origins should be strategically placed to allow blending of raw sugars with automatically controlled floor openings. Any low pol (less than 97.5) raw sugar with high moisture content should be blended and processed immediately to avoid inversion of sucrose even before the sugar leaves the warehouse.

B. Affination Station

Mingling syrup brix should be at about 72 with a maximum magma temperature of 42° C. The ratio of mingling syrup to raw sugar can be controlled by the wattage of the motor on the mingler. Belt weigher type control is maintenance intensive and should be avoided. Affination control can be based on color, ash and/or purity.

C. Melting Operation

It is recommended that the premelter be set for 72 brix and at a temperature of 70° C. The main melter should discharge the liquor at a temperature of 75° C and a minimum of 68 brix for maximum energy conservation. Normally, melting is accomplished by recycling vapor from the evaporators, etc.

D. Decolorization Process

For the most effective operation, the decolorization process chosen should be designed to give a fine liquor color of 200 maximum and an average of 150 color (ICUMSA method at 420 nm). The best choice for a decolorization scheme is carbonatation followed by ion exchange or granular carbon treatment. However, the ion exchange method is not environmentally friendly with respect to the waste disposal. Granular carbon suffers from high capital and operating costs, intensive maintenance, high sugar loss and low sulfate removal. However, the process is environmentally sound. The choice of either process

should be based on economical and environmental considerations, for both the present and future.

a. Flue Gas Treatment for Carbonation

The stack flue gas should be cooled to a maximum of 45° C. This is followed by a separate scrubber with a soda ash solution to remove most SO₂ contaminants. The gas compressor selected should be such that the temperature increase across the compressor be limited to 25° C. At any rate, the gas entering the “A” saturators should not exceed 85° C to minimize both chemical and physical sucrose losses and to avoid environmental problems.

b. Carbonatation

The retention time at the “A” saturators should be about 40 minutes and at the “B” saturator 20 minutes; therefore, two “A” saturators in parallel are needed. Some refineries are designed for four saturators; one as a spare for either “A” or “B” should the process be run for more than a month. If the refinery is to operate more than 300 days per year, the preferred mode of operation is to run 18 days consecutively and shut down for 3 days for maximum plant efficiency.

To avoid a sudden change in quality, remelt liquor is ratioed/metered into the washed sugar liquor. pHs should be around 9.6 and 8.3 for “A” and “B” saturators respectively when measured at 20° C. Some refineries minimize sucrose loss by operating “A” saturators at 75° C and reheating the liquor to 85° C prior to entering the “B” saturators.

Membrane press filtration should be used for desweetening the carbonate cake to reduce both the pol and percent moisture content in the cake. Low moisture levels (less than 30%) make it feasible for the cake to be used as a raw material for other industries. It goes without saying that a low percent moisture cake would save on freight costs.

It should be reiterated that carbonation is considered the best decolorizing process by many sugar technologists, assuming that the disposal of the carbonate cake is not a major problem. Carbonation, in addition to decolorization, partially removes SO₄, destroys invert, and maintains a higher liquor pH, all of which are beneficial to process efficiency.

c. Phosphatation

If the phosphatation process is selected, Tate & Lyle process technology's service is recommended. This is because T&LPT is considered the best in the sugar industry in the design of a phosphatation system.

d. Granular Carbon versus Ion Exchange

For a refinery with 1,000 ton per day capacity, in a granular carbon configuration, 8 columns 10' d x 42' h with each column carrying 2,400 cubic feet of granular carbon and a carbon regeneration kiln with a lot of peripheral equipment are required. In an ion exchange decolorization scheme, only 3 columns (each 8'd x 24'h) are required. The more equipment necessary to run the operation, the more manning and maintenance are expected, resulting in higher refining operating costs. However, a pulse bed granulator carbon system is preferred. Only two columns would then be needed.

The major disadvantage of the ion exchange resin process is the disposal of the dark colored sodium chloride effluent produced in the regeneration of the resin, and possibly waste resin itself in the future. One advantage of the ion exchange process is that it can remove up to 80% of the sulfate in the liquor. Sulfate normally causes pan scaling, resulting in potential product contamination, loss of refining capacity due to time spent removing the scale, high energy usage and high sucrose loss.

The operating and capital costs of the ion exchange process are about one half and one third of that of the granular carbon system, respectively. One disadvantage of the granular carbon system is the high sucrose loss associated with the process; the average sucrose loss is probably 0.04% on an operating day and as much as 0.3% during weekend shutdown periods.

Regardless of which technology is chosen, polishing filters are required before and after the decolorization process.

6. Evaporation

At minimum, a two-effect evaporator should be installed to produce a fine liquor (going to the pans) of at least 75 brix for energy conservation. The evaporating system should be designed to have excess vapor for re-use in vapor melting, heating of processing streams and air to the granulators and remelting the pan boiling, etc. Most refineries use vapor from the evaporator for sweetwater evaporation. A single effect thin film evaporator may cause product quality problems due to potential overburning of the sugar liquor. When overburning takes place, the resulting carbonaceous matter needs to be removed by a polishing filter again, to avoid contamination to the sugar products.

7. Sweetwater Evaporator

Many continuous refining process, such as decolorization, press filtration and dust collection from sugar drying, conveying and packaging, generate low density sweetwater. Water balance and the ability to orderly manage other continuous refinery processes are put at risk when upsets and down times occur in the raw sugar melting process, which would stop the orderly consumption of the low density sweetwater. It is for this reason that most well-run refineries have a

sweetwater evaporator to concentrate low density, highly colored material and to manage the imbalances that do occur.

Without a proper evaporating system to manage the water imbalance resulting from equipment failure or operators' error, the followings are likely to occur:

- A. Sweetwater and syrup containing a significant quantity of sucrose are allowed to accumulate on the lowest elevation in the refinery. Floor exposed to flooding will have to be replaced in time. Flooded floors are hazardous to employees. Also, spills are unsanitary.
- B. Continuous operations such as adsorbent/decolorization column desweetening and revivification will have to be interrupted. Without orderly regeneration of the adsorbent the quality of the final product and adsorbent itself will suffer.
- C. Large quantities of sucrose from sweetwater and syrups are dumped to the sewer. Not only will charges for sucrose losses be severe but the charges from the municipality to process the excess B.O. D. material will be expensive.
- D. The refining output (capacity) and product quality will suffer, resulting in loss of sales and customer dissatisfaction.
- E. The general sanitation of the facility will deteriorate over time if the spills cannot be cleaned up immediately. This is critical for maintenance of "Good Manufacturing" practices.
- F. Ultimately light density materials, such as sweetwater, have to be concentrated in the remelt boiling equipment. Orderly remelt boiling is time-consuming and can best be accomplished with a one strike boiling time of about four to six hours. When it is necessary to handle sweetwater, the performance of the recovery house, e.g., yield, will be severely affected.

8. White Sugar Boiling

A heat train through the vacuum pans, heat exchangers, evaporators and other refinery heating systems should be designed to recover a minimum of 80% of condensate with a good enough quality to be reused in the boiler house.

Over 60% of the energy usage in a refinery is consumed in the crystallization of sugar. A twenty-first century refinery should employ continuous sugar boiling, coupled with a vacuum cooling crystallizer to bring the total energy usage below 70 liters of No.6 oil per ton of raw sugar melted, with weekly shut-down, as practiced in the United States. The design of the whole system should be such that both conglomeration and coefficient of variation of sugar crystals is minimized.

With fine liquor color of 150, under normal conditions, #4 sugar should be sufficiently low in color to go forward to the final product without reprocessing it. #4 syrup purity is normally too high to be sent to the remelt house; therefore, it would be more advantageous to boil one

additional strike and remelt #5 sugar so that it can be combined with press filtered carbonated liquor before the polishing presses.

Vacuum pans should be of the short tube design with agitators to circulate the massecuite effectively. Additionally, an automatic seeding system should be installed at the pan floor to achieve the minimal manning requirement and consistent product quality. Whenever practical, surface condensers should be used for energy economy and BOD reduction.

9. Recovery Sugar Boiling

Affination syrup, #4 or #5 syrup and the concentrated excess sweetwater should be processed in a three stage boiling scheme. Sugar from the first strike should be sent forward to washed sugar liquor. Sugar from the second strike can also be sent forward, however, only after it has been double purged. Final sugar can either be sent forward or be used as a footing for the second strike after it has been double purged.

Double purging can be efficiently achieved by double purging centrifugal machines commonly used in beet factories in Europe. This scheme is particularly suitable for a fully automated refinery.

The conventional double Einwurf system requires frequent operator attention and is maintenance intensive. The system works quite well for a conventional refinery with much labor available, but it would not be conducive for a modern, fully automated refinery to meet the challenges of the 21st century.

10. Sugar Conditioning

Because of the weather conditions where most beet processors are located, and the purity and nature of the impurities present in the beet sugar, sugar conditioning techniques for beet sugar manufacturing may not be applicable for cane sugar conditioning.

Hot air entering the granulators should not exceed 90° C. Temperature of the sugar discharged from the granulators should not be greater than 45° C. It is recommended that sugar from the granulators be stored in holding bins for at least five hours but no more than seven hours before screening operations to remove fines and coarse sugars.

To prevent caking in bulk storage, the screened sugar should be placed in conditioning bins for at least twelve hours with conditioned air blowing through it. If a silo is used, sugar should be moved out from the bottom and recycled to the top of the silo during the shutdown day at six hour intervals.

11. Waste Water Treatment

For a modern refinery, treatment of streams having high B. O. D., high temperature and/or high solids content will be required on site. For an oxidation ditch type B. O. D. treatment to be successful, the cooling of hot streams such as contaminated condensates for optimum

microbiological activity will be necessary. Prior separation of any large quantity of suspended solids entering the B. O. D. treatment area will most likely to be cost effective. The key is to minimize the number of streams connected to the waste water treatment system.

12. Qualifications of Process Operators

To effectively operate a fully automated refinery, process operators should have a combination chemical, electrical and mechanical engineering Bachelor degree with a grade “B” average. A corporation can mitigate risk through organization design. Safety, environmental assurance, product quality, profitability and customer service level, are fixed by the kinds of organization management create.

This level of discipline training may be perceived as an unusually high skill level; however, it is not. As corporations meet their obligations to co-exist on a friendly basis with the community and to make a profit, the need to minimize and eliminate an operator’s errors becomes obvious. Operators’ errors are as much as one-half the reasons for serious incidents affecting operations, safety or environmental pollution. Given complex processes and systems, operators must be competent to detect small aberrations and proact before serious incidents or personal injuries occur.

Selection and training of process operators should begin as soon as possible. Only competent and responsible operators can ensure the highest process efficiency and enhance the profitability of the corporation.

CONCLUSION

In conclusion, the foregoing enumeration of the basic principles of cane sugar refining, the goals of cane sugar refining, and plant design requirements, if met, will result in an optimized operation that maximizes all the processes, produces high quality products within specifications, is profitable and environmentally friendly. In short, the company will be a good community neighbor and a successful corporation.

APPENDIX

The Basic Principles of Cane Sugar Refining

1. Sugar refining is a series of separations.
2. Once a separation has been made, good must not be added to bad, nor bad to good.
3. The best possible degree of separation must be secured from each separation.
4. The quality standards laid down must be achieved, but not appreciably exceeded.
5. Syrups should be stored cool and neutral, or slightly alkaline.
6. Heating of syrups and masses should be done as late and as fast as possible.
7. Stock in process should be as small as possible.
8. All processes should be carried out as fast as possible.
9. There should be as few processes as possible.
10. Each process should be as simple as possible.
11. Process units should be as large as is economical.
12. The addition of water to any sugar product should be held to a minimum.
13. It is better to thicken up lights by adding sugar than by evaporating water.
14. Sugar that has been crystallized out must not be redissolved.
15. The addition of ash to any part of the process makes molasses and loses money.
16. Reprocessing causes sugar destruction and incurs costs twice over.
17. Dry sugar should be subjected to the least number of water drops.
18. It is no use being technically correct if this results in losing money,
19. The cleaner the plant, the better the result.
20. A bad plant run by good operators is preferable to a good plant run by bad operators.

ELECTRODIALYSIS IN THE SUGAR INDUSTRY AS A PURIFICATION TECHNOLOGY

Dr Florence LUTIN - EURODIA INDUSTRIE SA – France

Abstract

Thanks to recent improvements in both the structure of anion-exchange membranes and in the design of stacks, electrodialysis (ED) can be considered one of the technologies that can help improve the cost effectiveness of sugar mills by: (i) control of organic fouling, (ii) operate at high temperature (up to 60°C), (iii) reduce waste effluents and pollution load, (iv) improve sugar yields, (v) reduce the volume of molasses, (vi) and save capital costs.

Operating results of a commercial plant in Europe after 4 years of operation are presented, along with a detailed material balance.

1. Introduction

Improvements in both the structure of anion-exchange membranes and the design of electrodialysis stacks have allowed electrodialysis to be considered as one of the technologies that can be introduced in the sugar industry to partially replace ion exchange resins for the demineralization and purification of sugar syrups.

Until a few years ago, the two main limitations of electrodialysis in the sugar industry were the short membrane life, especially for the anion-exchange membranes, and the low operating temperature that had to be maintained below 40°C.

The recent development of a new anion-exchange membrane, (the NEOSEPTA[®] AXE 01 from TOKUYAMA Corp.) that can be cleaned with a high NaOH concentration and operated at temperatures up to 60°C, has made it possible to minimize organic fouling. Consequently, the operating costs are reduced.

2. Improvement of the electrodialysis technology

2-1 A new Neosepta anion-exchange membrane

To economically operate ED in the sugar industry, one of the key challenges is to use an anion-exchange membrane that is resistant to organic fouling. Until recently, the AFN Neosepta membrane was the most suitable membrane thanks to a low cross-linking, allowing easy

transport of organic anions of molecular weight lower than 300. However, this membrane showed a weak mechanical resistance when cleaned with NaOH at high temperature.

The AXE 01, a new anion-exchange membrane, has been developed by Tokuyama Corporation for sugar applications to overcome the above limitations. Table 1 gives the characteristics of the new AXE 01 membrane, compared to the AFN.

Table 1. Characteristics of the new AXE 01 membrane, compared to AFN.

NEOSEPTA ANION MEMBRANE	AXE 01	AFN
Electrical resistance (ohm.cm^2)	1.4	0.3-1.0
Exchange capacity (meq.g^{-1})	2.0	2.5-3.7
Burst strength (Mpa.cm^{-2})	0.41	0.2-0.35
Thickness (mm)	0.17	0.15-0.18

Thanks to its higher burst strength, this membrane is easier to handle in industrial ED stacks.

2-1-1 Alkali resistance

To increase membrane life, it is necessary to avoid irreversible organic fouling by opening the polymeric channel with a low DVB content. In addition, it is beneficial to have the possibility of cleaning with a high concentration caustic solution to allow membrane swelling and remove organic molecules trapped inside the membrane. Indeed, when cleaning ion-exchange membranes with caustic, a risk exists of reducing the exchange capacity and the mechanical resistance of the membrane.

The AFN and AXE 01 membranes have been soaked in 1wt% NaOH + 1wt% NaCl solution during 5 days at 60°C. The exchange capacity and burst strength were measured (Table 2).

Table 2. Exchange capacity and burst strength of AFN and AXE 01 after treatment with NaOH.

NEOSEPTA ANION MEMBRANE	AXE 01		AFN	
Soaking time in 1%NaOH solution-60°C	0	120 h	0	120 h
Exchange capacity (meq.g^{-1})	2.0	1.8	3.1	0.3
Burst strength (Mpa.cm^{-2})	0.41	0.32	0.3	0.1

The new membrane features a high alkali resistance with only a 10% E.C. and a 22% burst strength decrease, compared to 90% and 67% for the AFN.

2-2 Operating temperatures up to 60°C

Operating at temperatures higher than 40°C minimizes the growth of microorganisms, especially in the sugar industry where fermentation can start very rapidly. Together with conventional cation-exchange membranes, the AXE 01 can be operated at up to 60°C. In the meantime, new spacers have been developed with new polymeric materials offering perfect mechanical stability at up to 60°C.

3. Demineralization rate and sugar purity

Several pilot trials have been carried out with cane and beet sugar syrups in order to evaluate and optimize the demineralization rate that can be achieved with ED.

3-1 Demineralization of cane sugar molasses (Morocco)

- Feed : 30 Bx and 50 Bx molasses
- Operating temperature : 50°C
- Pilot stack : EUR2B-10 – 0.2 m² – NEOSEPTA AXE 01 and CMX membranes

The purpose of this trial was to evaluate the demineralization rate for syrup concentrations at 30 and 50 Bx. At 30 and 50 Bx, for current and conductivity as a function of the treatment time, we have obtained a good reproducibility over 4 runs at each concentration (figures 1-2-3-4).

In both cases, cane sugar molasses can be demineralized by electrodialysis at up to 60%.

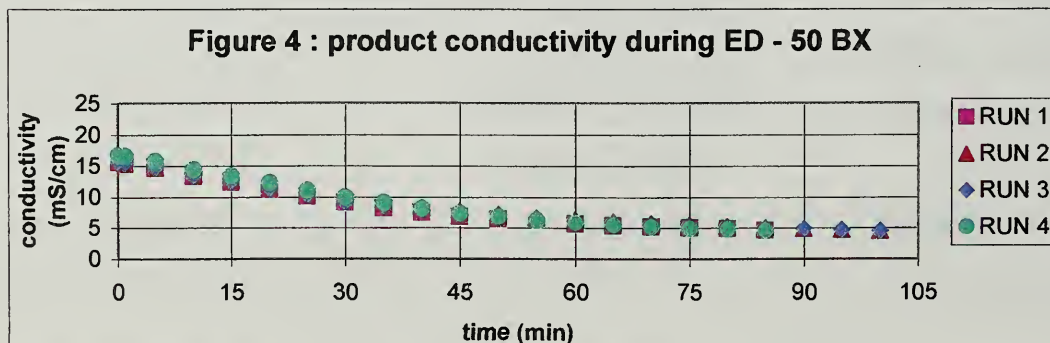
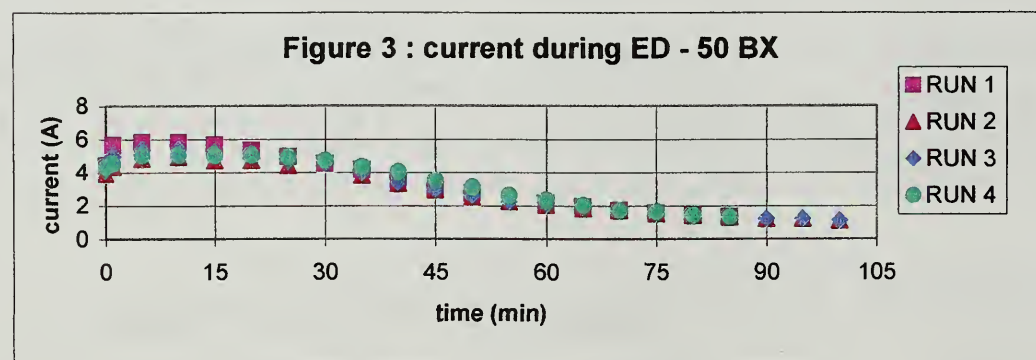
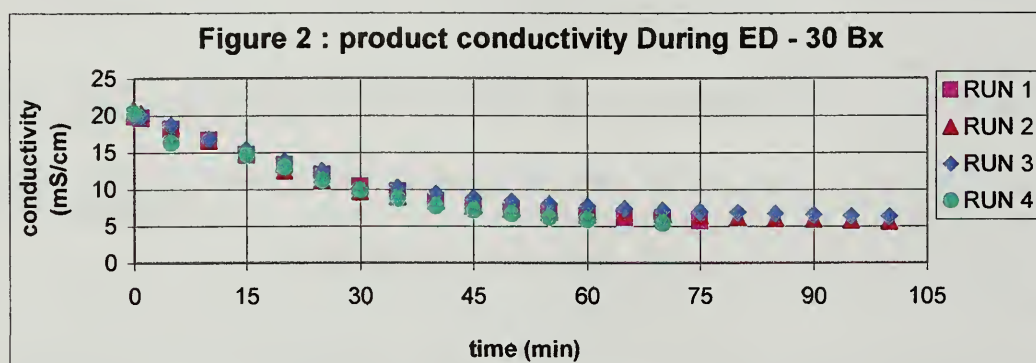
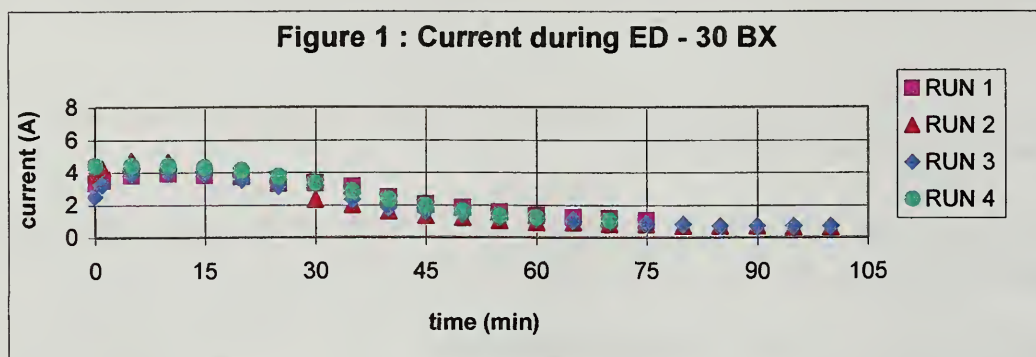
The overall demineralization rate is independent of the concentration of the molasses. At the same voltage, the applied current density is directly proportional to the cations concentration in the molasses (Table 3). The demineralization capacities are 3.5 eq.h⁻¹.m⁻² at 30 Bx and 4.5 eq.h⁻¹.m⁻² at 50 Bx.

Table 3.

	30 Brix	50 Brix
Conductivity decrease (%)	70	70
Total Cations removal (%)	65	55
Ca ⁺⁺ , Mg ⁺⁺ removal (%)	60% Ca ⁺⁺ 50% Mg ⁺⁺	35% Ca ⁺⁺ 30% Mg ⁺⁺
K ⁺ , Na ⁺ removal (%)	75% K ⁺ 25% Na ⁺	75% K ⁺ 45% Na ⁺
Demineralization capacity	3.5 eq.h ⁻¹ .m ⁻²	4.5 eq.h ⁻¹ .m ⁻²
Current Efficiency (%)	90	90

DEMINERALIZATION OF CANE SUGAR MOLASSES - Morocco

Electrodialysis at constant voltage : 0,8 V/cell. - EUR2B-10 pilot



The divalent cations (calcium and magnesium) appear more easily removed from molasses at 30 Bx than at 50 Bx. In the meantime, the potassium and sodium removal rates are higher for 50 Bx molasses than for 30 Bx molasses.

Nevertheless, for industrial plants, the most important limiting factor regarding product concentrations is the difference of syrup viscosity between 30 and 50 Bx, and consequently the pressure drop through the stacks. For this reason, working with 30 Bx seems more convenient, if it is acceptable from the point of view of the overall energy balance.

3-2 Purification of beet sugar syrup

This pilot test is interesting with respect to the minerals and organics removal rate.

Beet sugar syrup can be demineralized by ED at up to 80%. However, to avoid inversion, the pH must be maintained above 7, and, therefore, the demineralization rate must be limited to 68%. The ion removal capacity is $3.6 \text{ eq.h}^{-1}.\text{m}^{-2}$.

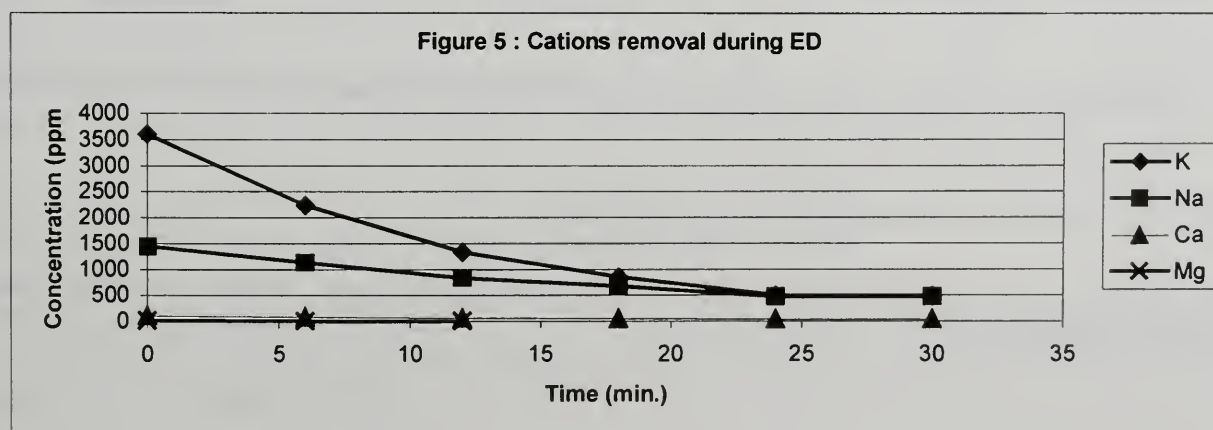
♦ Operating conditions:

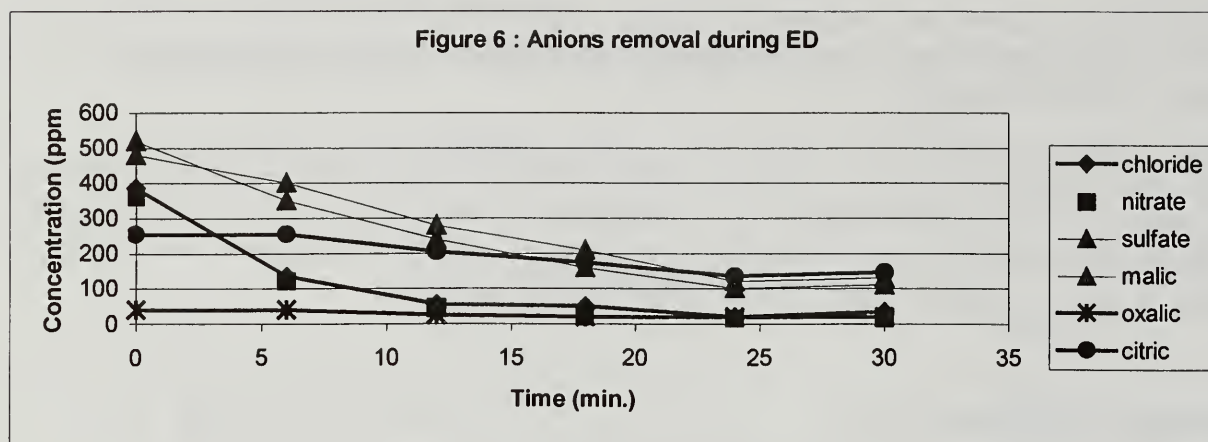
Pilot stack : EUR2B-10 – 0.2 m^2 – Membranes : AXE 01 / CMX
 Temperature : 25°C
 Current density : 11 mA/cm^2 – 1 Volt/cell
 Brix : 30 Bx – pH: 8.6 - initial conductivity : 6.8 mS/cm – Final cond : 2 mS/cm

Ions Removal rate :

CATIONS	% Removal	ANIONS	% Removal	ORGANICS	% Removal
K ⁺	87	HCO ₃ ⁻	66	Malic	57
Na ⁺	68	Cl ⁻	87	Citric	32
Ca ⁺⁺	75	SO ₄ ²⁻	70	Oxalic	51
Mg ⁺⁺	51	NO ₃ ⁻	95		

Kinetics of transport





The kinetics of potassium transport is higher than sodium transport (Figure 5).

Figure 6 shows the removal of organic acids through ED. Malate and citrate anions can be transported easily through the anion-exchange membranes. The transport rate of malates is the same than for sulfates.

3-3 Demineralization of liquid sugar

A fructose syrup has been demineralized up to 50%.

♦ Operating conditions:

Pilot : EUR2B-7 – 0.14 m² – Membranes : AXE 01 / CMX
 Temperature : 30°C
 Current density : 7 mA/cm² – 1 Volt/cell
 Brix : 30 Bx - initial conductivity : 8 mS/cm – Final cond : 4 mS/cm

In these conditions, the demineralization capacity is 18 L.h⁻¹m⁻² with a 53% conductivity decrease.

At higher temperature 50°C and same voltage, current density increases up to 12 mA/cm² and demineralization capacity becomes 31 L.h⁻¹m⁻².

The syrup purity is improved from 85% to 90 % (Table 4).

The sugar losses into the brine are lower than 0.5 % of the initial sugar content, it means that sugar recovery reaches 99.5%.

Table 4.

Composition	Feed	Demin. Syrup
Genuine Brix	30.0	28.1
Total Sugar (g/kg)	255	253.72
Non-sugar (g/kg)	45	27.4
• Minerals (g/kg)	31	15.5
• Others (g/kg)	14	11.9
Purity (%)	85	90
Sugar recovery (%)		99.5

If we increase the demineralization up to 70 %, purity increases from 90% to 93%

4. Operating results of a commercial plant

The first commercial ED plant in the European sugar industry in has been operating since 1996. The target was to double the existing capacity of the ion exchange resins without any increase of the pollution load.

Electrodialysis has been chosen to demineralize the juice at up to about 55% and keep the same volume of existing resins as a “polishing” step.

The feed at 12 or 24 Bx is demineralized with 12 stacks arranged in 3 lines in parallel (each line has 4 stacks in series), thus achieving a 55% conductivity reduction.

Each line treats 20 m³/h. With 4 stacks EUR20-440 in series, the conductivity is reduced from 8 down to 4 mS/cm. The maximum pressure drop through the four stacks operated in a single pass is 4 bars.

The throughput is 5 eq.h⁻¹.m⁻². The single pass reduces the residence time and avoids any bacterial development. For the 1999 sugar campaign, the new AXE 01 membranes and new spacers have been installed to operate at 55°C: during this campaign, no increase of pressure drop was observed while the demineralization rate was dramatically improved.

Since then, the EUR40, a new size of ED stack, is available: such a stack would result, if used for demineralization at 60%, in only 2 stacks in series per line.

The sugar losses are less than 0.5% of the sugar production. The electrical consumption is 1.1 KWH/m³ for ions transport and pumping. CIP consumes only 0.045 L/m³ of HCl at 0.4% and 0.001 L/m³ of NaOH at 0.4%.

The waste flow rate is approx. 26 m³/h with a minerals content of 0.1 eq/l. The capital cost for a capacity of 40 m³/h is 1 700 000 Euro with a membrane replacement cost lower than 3000 Euro/m³/year.

5. Conclusion

With new available technology that can operate at up to 60°C, electrodialysis can be considered as one of the technologies that can contribute to improve the cost effectiveness of sugar plants, since it can help to:

- control organic fouling,
- reduce waste effluents and pollution load,
- improve sugar yields,
- reduce the volume of molasses,
- save capital costs.

PHANEORCHAETE CHYRSOSPOSIUM IMMOBILIZATION FOR CONTINUOUS TREATMENT OF ION EXCHANGE RESINS EFFLUENT

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ABSTRACT

Adhesion of *Phanerochaete chrysosporium* to various solid carriers was studied. Amount of immobilized mycelium was higher for porous and rough (polyurethane foam; Scotch-Brite™ and Poraver™) than for nonporous and smooth carriers (polyvinylchloride and stainless steel). Mycelia were significantly more active when immobilized on porous/rough carriers. These results were attributed to the roughness effects of solid surfaces as well as porosity, which protect cells against the detrimental effects of shear stress.

The ability of *P. chrysosporium* immobilized on polyurethane foam (PUF) and on Scotch-Brite™ (SB) to treat the effluent efficiently for a long-term operation was confirmed. Decolorization efficiencies of 67% and 63% and phenolics reduction of 65% and 63% were achieved for PUF and SB, respectively, during the repeated-batch tests conducted for 31 days.

INTRODUCTION

Anion-exchange resins are used to decolorize sugar liquor in the refining process. During the first part of Sacharate Regeneration of resins (Bento, 1996), a solution of 35 g/l CaCl₂ is used, giving rise to an effluent which represents an environmental problem due to the presence of phenolic compounds, intense coloration and high organic load (COD). The high toxicity of phenolic compounds to living organisms is well reported in literature (Borneff, 1978; Dean, 1978). The brown color of the effluent is not only aesthetically unacceptable but also inhibits the natural process of photosynthesis in natural waters leading to a chain of adverse effects on the aquatic ecosystem. The organic load can be eliminated, at least in part, using traditional biological treatments but the compounds responsible for the intense coloration are poorly degraded by the organisms normally involved in these treatments (Ohmomo *et al.*, 1987).

The white-rot fungus *Phanerochaete chrysosporium* is a potentially useful microorganism in waste treatment systems because it is able to degrade a broad spectrum of structurally diverse organic compounds. Evidence suggests that the unique ability of *P. chrysosporium* to degrade those compounds is due, at least in part, to the lignin degrading enzymatic system of this microorganism that is non-specific and partially extracellular (Bumpus *et al.*, 1985; Bumpus and Aust, 1987; Barr and Aust, 1994).

Previous studies undertaken in our laboratory demonstrated that *P. chrysosporium* was able to degrade the main colorants present in the effluent (Guimarães *et al.*, 1999). In order to have an effective continuous effluent treatment with *P. chrysosporium*, a bioreactor has to be developed in which the fungal cells can grow well and maintain high activity to degrade the effluent for a long term operation. A promising method to accomplish this goal lies in the immobilization of the fungus in an appropriate solid carrier. In this work we studied the adhesion of *Phanerochaete chrysosporium* to various solid carriers: polyurethane foam, nylon web (Scotch-Brite™), foam glass (Poraver™), polyvinylchloride Rashig rings, and stainless steel Rashig rings. The ability of the immobilized cultures to treat the effluent in a long-term operation was evaluated.

MATERIALS AND METHODS

Effluent

The effluent was collected during the first part (with 35 g/l CaCl_2) of Saccharate Regeneration of ion exchange resins. Before being used in the experiments, the effluent was adjusted to pH 4.5 and supplemented in order to have the final composition in culture medium (per liter): 10g glucose; 2.0g KH_2PO_4 ; 1.06g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 10 ml mineral solution; 10 ml thiamine solution (1 mg/l). The mineral solution was based on the one described by Tien and Kirk (1988), but contains 60 μM Mn(II).

Microorganism and inoculum

P. chrysosporium (ATCC-24725) was maintained at 4°C on 2% malt extract agar. Inoculum consisted of a homogenized mycelial suspension, grown in liquid cultures for 48h (Tien and Kirk, 1988).

Adhesion tests

All tests were made in triplicate in 250 ml flasks containing 36 ml effluent plus 4 ml inoculum. Carriers listed in Table 1 were placed in the flasks, a net volume of 0.75 L solid carrier /L culture medium was used. Cultures with free cells were run in parallel in the same conditions.

After 8 days incubation (38°C, 60 rpm), solid carriers were rinsed with water in order to eliminate all nonadhering mycelium. Immobilized and nonimmobilized mycelium were measured in terms of dry weight, at 105°C overnight, of mycelium after filtration through a tared filter. Carrier dry weight was subtracted from the weight of carrier plus mycelium. Color and phenolic compounds concentration of the effluent were measured at day 0 and 8 for evaluation of biodegradation activity.

Table 1 – Solid carriers used in *P. chrysosporium* adhesion tests

Carrier	Shape	Size (mm)
Stainless steel (SS)	Rashig rings	$\varnothing = 1.0$, L = 1.0
Polyvinylchloride (PVC)	Rashig rings	$\varnothing = 1.0$, L = 1.3
Foam Glass - Poraver™ (POR)	Spheres	6.3–6.7
Polyurethane Foam 20 Kg/m ³ (PUF)	Cubes	5 x 7 x 7
Nylon Web – Scotch-Brite™ (SB)	Cubes	6 x 7 x 7

Repeated-batch biodegradation tests

In these tests only PUF and SB carriers were used. Fungus was allowed to grow on the supports during 8 days in the presence of effluent (Growth phase). The effluent was then replaced by a fresh one, starting the biodegradation phase (batch I). After that, effluent was replaced at specific time intervals. Eight batches were conducted during 31 days. In the last two batches Tween 80 was added at a final concentration of 0.1% (v/v).

Analytical procedures

Phenolics were determined using Folin and Ciocalteu reagent (Clarke *et al.*, 1985). Color was measured as attenuation at 420 nm, after pH adjustment to pH 9.0 with borate buffer. Scanning electron microscope (Leica Cambridge S360, Netherlands) was used to observe the morphology of solid carrier surfaces and colonization. Before examination, samples were dried and coated with gold.

RESULTS AND DISCUSSION

Adhesion tests

Results of adhesion tests are summarized in Table 2. Fungal adhesion was observed in all carriers tested. However, percentages of immobilized mycelium were higher in cultures containing porous carriers (POR, PUF or SB) as compared to non-porous carriers (SS and PVC). Concerning effluent biodegradation activity of immobilized mycelia, i.e. decolorization and phenolic compounds reduction activity, it was observed that mycelia were significantly more active when immobilized on porous supports (POR, PUF and SB). It was also observed that, in these conditions, non-immobilized cells were not capable of performing any biodegradation at all, confirming the importance of immobilization.

SEM (Scanning Electron Microscopy) examination of solid carriers surface morphology showed that POR, PUF and SB were rougher than SS and PVC (Fig. 1). We can also observe that in porous carriers (POR, PUF and SB) fungus grow inside the pores, being protected against hydraulic shear forces.

There are many reports in the literature about the advantages of using porous and rough supports for biofilm development. Apart from displaying a high surface area, a rough surface and/or internal pore space may provide a more hydrodynamically quiescent environment, thereby reducing the detachment of immobilized cells by hydraulic shearing forces (Bryers, 1987; Characklis, 1990; Quirynen and Bollen, 1995). This is in agreement with our findings.

It is known that *P. chrysosporium* ligninolytic enzymes are very sensitive to shear stress (Kirk et al., 1978; Faison and Kirk, 1985). Immobilization of *P. chrysosporium* in porous and rough carriers may protect the enzymatic system against the detrimental effect of shear forces, thereby improving fungus activity. This can explain the high activity observed in cultures containing mycelia immobilized on POR, PUF and SB.

We chose PUF and SB for further studies. POR was rejected due to its sensitivity to erosion - breaking was observed during the experiments.

Table 2 – Percentage of immobilized mycelia, decolorization activity and phenolic compounds reduction activity for *P. chrysosporium* immobilized on stainless steel (SS), polyvinylchloride (PVC), Poraver™ (POR), polyurethane foam (PUF) and Scotch-Brite™ (SB) as compared to free cells, after 8 days of total incubation.

Carrier	Immobilized mycelia (%)	Decolorization (%)	Phenolics Red. (%)
SS	87.7	6.8	20.6
PVC	85.1	11.6	21.4
POR	97.0	44.9	64.2
PUF	94.0	46.6	62.2
SB	96.6	49.8	64.6
Free cells	—	7.3	2.8

Repeated-batch biodegradation tests

The longevity of the degradation activity of *Phanerochaete chrysosporium* immobilized on polyurethane foam (PUF) and on Scotch-Brite™ (SB) was measured in repeated-batch tests. Biodegradation activity was measured in terms of decolorization and reduction of phenolic compounds.

Cultures immobilized on PUF or SB behave similarly, as we can see in Figs 2 and 3, respectively. The time needed to obtain significant degradation has been reduced from 8 days (first batch) to 3 days (third batch). This means that the biomass activity had increased, thereby reducing the processing time. Therefore, the following batches were conducted for 3 days each. In the last two batches, Tween 80, a biological detergent, was added to the cultures, to assess the possibility of improving fungal activity, as is reported by several authors (Jager *et al.*, 1985; Asther *et al.*, 1988). No effect was observed in the first batch. However, in the second one a significant increase in decolorization activity was observed, from 62% to 78% for cultures with PUF (Fig. 2) and from 58% to 72% for cultures with SB (Fig. 3). Concerning phenolic compounds reduction activity, there was only a slight improvement. Further studies have to be done in order to clarify the effect of Tween 80.

During the 31 days of repeated-batch tests, decolorization efficiencies of 67% and 63% and phenolics reduction of 65% and 63% were achieved for PUF and SB, respectively (Fig. 2 and 3). The fungus maintained a stable degradation for a long time. The results demonstrate that *P. chrysosporium* immobilized on polyurethane foam (PUF) and on Scotch-Brite™ (SB) is able to treat the effluent efficiently in a long-term operation.

We were able to reduce significantly the time needed for effluent treatment when compared with static cultures.

The results point out to the possibility of operating continuously, which is positive in wastewater treatment systems. In a near future, a bioreactor operating continuously will be tested.

ACKNOWLEDGMENTS

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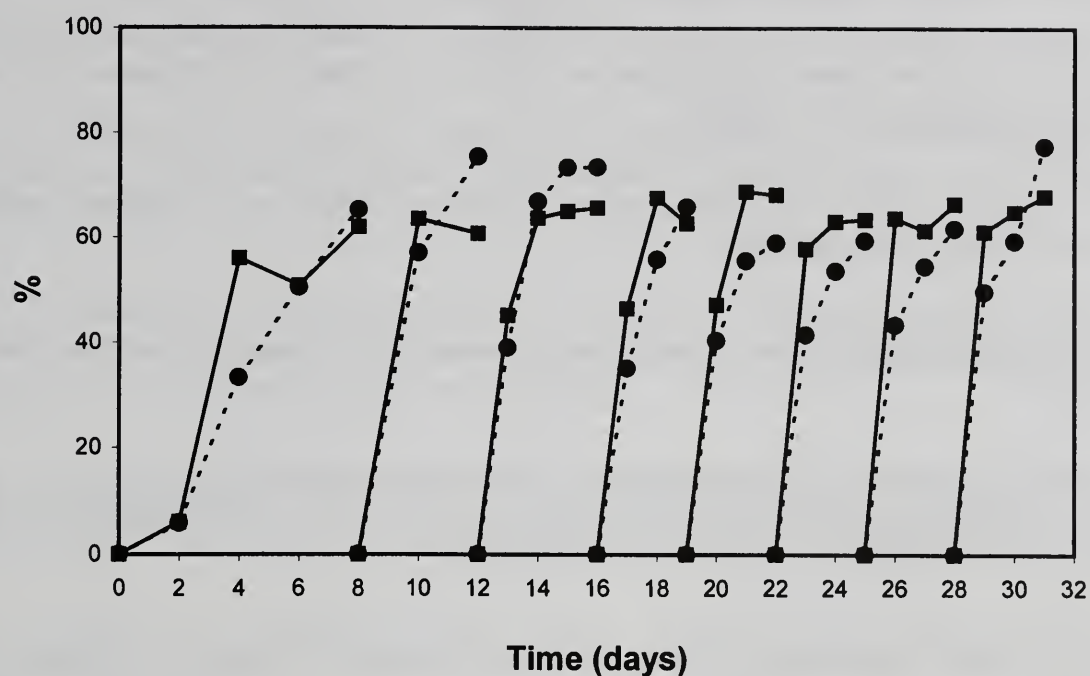


Figure 2 - Decolorization (●) and phenolic compounds reduction (■) obtained in repeated-batch tests with *P. chrysosporium* immobilized on polyurethane foam (PUF).

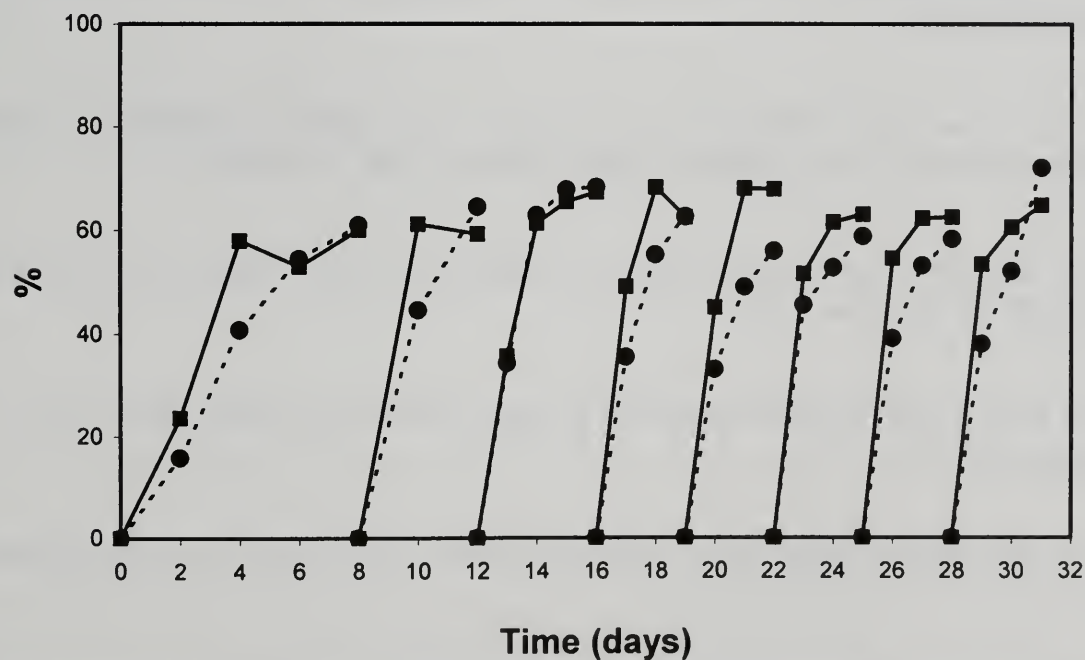


Figure 3 - Decolorization (●) and phenolic compounds reduction (■) obtained in repeated-batch tests with *P. chrysosporium* immobilized on Scotch-Brite™ (SB).

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PROCESSING OF FROST DAMAGED BEETS AT CSM AND THE USE OF DEXTRANASE

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Abstract

The sugar beet campaign of 1998 in the Netherlands suffered from severe weather conditions; i.e. subsequent periods of plentiful rainfall, frost and thaw. Thus, the harvest and processing quality of the beets became troublesome, which affected the processing capacity of the sugar factories. This paper will focus on the processing of frozen respectively thawed beets.

A high-performance liquid chromatography method (HPAEC-PAD) was rapidly developed in order to be able to monitor the degree of deterioration of the frost-damaged beets. Both the invert sugar and dextran levels were analysed daily in raw juice samples. About 10 days after the outdoor temperature came again above 0 °C, the concentration of both sugar types sharply increased, thus causing processing problems.

Even at relative low levels of dextran in raw juice (i.e. 75 mg/l), the filtration rate of the 2nd carbonation slurry dropped markedly and, consequently, the slicing capacity decreased to 50%. The dosage of 10 ppm dextranase NOVO 50L enzyme to the extraction appeared to be sufficient to restore the slicing capacity to 90% of the nominal capacity.

In fact, it was the high level of invert sugar in thawed beets (up to 4 g/l in raw juice !) which made the processing of this low-quality beet material most uneconomic. The high invert sugar content consumed (in juice purification) a lot of alkalinity, which could only be compensated by the addition of excessive amounts of caustic soda. Nevertheless, both the juice quality became very moderate (e.g. low juice purity, high lime salts content, high juice as well as sugar colour) and the amount of sugar that ended up in the molasses reached an unacceptable high level.

Introduction

Deterioration of sugar beets due to freezing and subsequent thawing is a well-known, but undesired phenomenon in sugar beet processing (Sugar Technology, 1998). When sugar beets freeze, the cells are disrupted and, upon thawing the beets become susceptible to attack by micro-organisms. In particular, *Leuconostoc mesenteroides* is responsible for the consumption of sugar for the production of dextran.

Dextran (a glucose polymer with α -1,6 linkages in a straight chain, with branches at the C3 and/or C4 position) is formed by a transglucosylation reaction from sucrose, which concomitantly results in the release of fructose as monomeric reducing sugar. The dextran polysaccharide enhances the viscosity of the process juices and affects the crystallisation of both calcium carbonate in juice purification and slightly that of sucrose in the sugar house as well. The interference of dextran with the crystallisation of calcium carbonate so that very fine crystals are formed, is thought to cause the major problem of the processing of frost-damaged beets. The dextran problem usually becomes apparent first in a troublesome filtration of the second carbonatation precipitate (Barfoed and Møllgaard, 1987; Oldfield, Dutton, Teague and Williams, 1975; Stoppok and Buchholz, 1994).

In the past, several proposals have been made to tackle the dextran problem by specific adaptations of the traditional lime-carbon dioxide beet juice purification (Buczys, 1994; Grabka and Wasiak, 1995; Oldfield, Dutton, Teague and Williams, 1975; Palmer and McCarey, 1981), which, however, are just attempts to counteract the symptom. The dosage of dextranase, on the other hand, enables the complete elimination of the cause of the problem: the endo-dextranase enzyme hydrolyses the dextran into low molecular weight dextran chains and after sufficient reaction time, the eventual main break-down products will be iso-maltose and iso-maltotriose. These low molecular weight dextran fragments are considered to be harmless for the further processing of the beet juices, as has been confirmed from practical experiences (Barfoed and Møllaard, 1987; Stoppok and Buchholz, 1994).

Due to the poor weather conditions in the Netherlands during the sugar beet campaign of 1998, CSM Suiker bv was confronted with the processing of frozen beets and, subsequently, of frost-damaged (i.e. thawed) beets. This paper describes the way we have encountered the technological difficulties of processing frost-damaged beets. It includes a short explanation on the weather conditions during the harvest period, which eventually has caused the problem. Then, the applied analytical procedures, which we have developed in order to enable the “real time” monitoring of the extent of the dextran problem, will be dealt with. Finally, the technological consequences for the process, e.g. effect on slicing capacity, juice quality, sugar to molasses, as well as the measures taken (with a focus on the usage of dextranase) will be discussed.

Harvest conditions during the 1998 Dutch sugar beet campaign

Because of its location by the sea, the Netherlands has a marine climate; i.e. usually moderate temperatures and pretty much rainfall over the year. At late autumn, during the sugar beet campaign, there always is the risk of frost. We therefore strongly recommend the farmers to harvest the sugar beets before mid-November. Then, if necessary, they can protect the beets from the cold, and thus against frost damage, by properly covering the beet clamp by plastic sheet.

Due to an excessive rainfall in the period of 27 October to 8 November, 1998, the farmers were not able to harvest the amount of beets required by the sugar factories for processing. As a consequence, CSM Suiker had to reduce the slice rate in this period to 50-60% of its nominal capacity. Additionally, the recommended harvest of all beets before mid-November could no

longer be achieved by the farmers. To make matters worse, within two weeks after the rainy period, it started to freeze in the Netherlands, which lasted until 5 December. Nevertheless, there were just enough beets available to keep the factories going. The reduced rigidity of cossettes from frozen beets slightly influenced their processing; a slicing capacity of about 90% could be maintained.

From 5 December on, when the thaw set in, we expected processing problems due to microbial dextran formation after about 10-14 days according to the literature (Barfoed and Møllaard, 1987; Sugar Technology, 1998). A typical example of a sugar beet which has been frozen at the top when it was still standing in the ground is shown in Figure 1.

Figure 2 illustrates the course of the outside temperature from mid-November 1998 until the end of the campaign. It shows that a first frost period from 21-25 November was rapidly followed by a second frost period from 30 November to 5 December. Apparently, the thaw period in between had been too short, and the temperature too low, to develop a dextran problem for the factories (see below).

Analytical monitoring frost problem

Rapid colorimetric test for invert sugar in beet brei extracts.

Measurement of invert sugar can be used to detect deteriorated, e.g. frost-damaged, beets. In the past, a rapid invert test was developed (Oldfield, Dutton and Teague, 1970), which is considered to be quite adequate as a means to distinguish between invert levels of <1.0, 1.0, 1.5, 2.0, respectively >2.0g invert per 100g sugar in beet. By adding tetrazolium reagent to a beet brei extract and subsequent brisk heating (1 min) in a boiling water bath an either colorless or a turbid red suspension is developed, depending on the invert level of the sample. The sample color is visually compared with standards, which then gives a rough, semi-quantitative, approximation of the invert concentration of the beet. In Figure 3 an unknown sample is compared to the invert standards, from which it can be concluded that the sample has a invert level between 1.0 and 1.5g per 100g sugar. The invert level in fresh and well-clamped beet normally is below 1.0 g per 100g sugar (Oldfield, Dutton and Teague, 1970).

This simple method is very suitable to perform in the tare house and can be completed within 3 minutes.

HPAEC-PAD analysis of invert sugar and dextran.

The Dionex CarboPac PA1 column (250x4.0 mm), preceded by a guard column (50x4.0 mm) was used for the determination of both the invert sugar and dextran concentration in raw juice samples. A special sample pretreatment was developed in which a rapid hydrolysis of dextran into particularly isomaltose and isomaltotriose is attained. This enabled the simultaneous, i.e. one run, chromatographic separation of invert sugar and the small dextran fragments.

For that purpose, to a sample of 100ml raw juice, 10µl dextranase NOVO 50L enzyme was added, homogenised and incubated in a closed bottle for 1 hour in a water bath at 55 °C. The sample was cooled to room temperature, diluted by 25 times and filtered through 0.45µm: 25µl

of this pretreated sample solution was injected into the HPAEC-PAD system for analysis. Both the enzyme concentration and length of the incubation time were sufficient to completely hydrolyse the dextran: as checked with several pure dextran preparations of different chain length, isomaltose and isomaltotriose were obtained from dextran with about 67% yield. Thus, knowing this yield factor, the original dextran concentration in raw juice samples could be calculated.

The high-performance anion exchange chromatographic (HPAEC) separation was achieved by isocratic separation with 250mM NaOH on the above-mentioned column and a flow rate of 1.0ml/min. The different saccharides were detected by a Dionex ED40 Electrochemical detector in the pulsed amperometry mode (PAD).

Stock solutions of pure glucose and fructose (Fluka, 49139, resp. 47739; both 0.5g/l; 25 times diluted prior to injection), respectively isomaltose and isomaltotriose (Sigma, I-7253, resp. I-0381; both 0.125g/l; 10 times diluted prior to injection) were prepared and used for calibration of the detector response.

According to this procedure, quantitative data of both the invert sugar and dextran level could be obtained within 2 hours after a raw juice sample was taken. Thus, we were able to monitor the quality of the incoming beet material almost without any delay. We have used this to decide whether or not it was necessary to add dextranase to the process. This would not have been possible without using the new analytical procedure, and with only having available the conventional time-consuming and cumbersome methods of polysaccharide determination, e.g. alcohol precipitation of polymers, followed by colorimetric analysis of saccharides.

Course of invert sugar and dextran in the processed beet material.

After the end of the frost period, we started at 8 December in the tare house to monitor the invert level by the rapid colorimetric test. In the day time we analysed 50-100 different beet brei extracts per day, which gave a good general impression of the incoming beet quality. Figure 4 gives an overview of the data which have been gathered until the end of the campaign; only the percentage of those beet brei samples with an invert level higher than 1.0g per 100g sugar is shown. In other words, the length of the bars in Figure 4 represents a measure of the amount of deteriorated beets to be processed. Beets with invert >2.0g per 100g sugar, indicated by the black part at the top of the bars, are considered to be seriously frost-damaged, but already a significant concentration of dextran may be expected at an invert content of 1.5-2.0g per 100g sugar (Oldfield, Dutton and Teague, 1970). From Figure 4 it can be concluded that around 15 December the frost damage (i.e. dextran) problem became apparent.

With the HPAEC-PAD method a more precise quantitation of the frost damage is obtained. Already at the end of the first frost period we started in CSM factory 1 with monitoring both invert sugar and dextran by this method. As is illustrated in Figure 5, it lasted until 14 December before we first detected any dextran present in raw juice, but still at a rather low level of 50-75mg/l. Then, three days later the dextran content in raw juice appeared to increase exponentially and reached a maximum level of 650mg/l at 20 December, after which it dropped to about 400mg/l. The invert sugar content followed more or less the same trend as that of dextran: a

constant level of around 1.5g/l until 15 December and a subsequent sharp increase to 3.5-4.0g/l. These findings are in agreement with those of the rapid invert test, mentioned above.

We also recorded the invert sugar and dextran content of the raw juice from CSM factory 2 (data not shown), which were similar to those of the factory 1: i.e. sharp increase of both invert and dextran around 15 December. Fortunately, by then factory 2 had processed almost all the allocated beets and only at 18 December, the last day of their campaign, did they encounter significant dextran problems.

Technological consequences for the sugar manufacturing process

The slicing capacity of a sugar beet factory usually gives a good impression whether the process is running smoothly or if it is frequently facing problems. Figure 6 records the slicing capacity chart of factory 1, starting a few days before the dextran in raw juice became apparent until the end of the campaign. During the first days, at the beginning of the chart, factory 1 received and processed partly frozen/thawed beets, which, due to a slight loss of firmness, could be processed at about 90% of the nominal capacity. No dextran problems occurred in that period. A technical failure at 14 December, i.e. interruption of the power supply, temporarily caused a drop in the processing which could be more or less restored after repair. But then, on 16 December, factory 1 faced the first real dextran problems located at the filtration of the second carbonatation slurry. Several attempts were made to improve the throughput in the juice purification, e.g. increased alkalinity of the main liming, addition of lime to second carbonatation. Although temporarily an increase of the slicing capacity seemed to happen, in the long run all measures failed to solve the dextran problem (already at a dextran level in raw juice of approximately 100mg/l).

On 17 December again the capacity dropped to 50%. We then analysed an enhanced dextran level of 200-300mg/l in raw juice samples, which supported our decision to start the addition of dextranase NOVO 50L to the process. The enzyme was continuously pumped into the cossettes-juice mixture which is leaving the countercurrent mixer and, subsequently, enters the tower at the bottom. In order to prevent a too rapid thermal inactivation of dextranase, the temperature of the circulation juice was decreased from 80 to 65 °C. Almost immediately after the start of the dextranase addition the slicing capacity could be recovered almost to normal. From then on till the end of the campaign 10ppm dextranase solution on juice was added, which caused an additional processing cost of about 0.40 Euro per ton beet. The two short capacity drops to 70%, as shown in the chart of Figure 6, were the result of an accidental interruption of the enzyme dosage to the process; the first time caused by electrical failure of the dosage pump; the second time due to a too late notice of an empty dextranase container. Anyway, it underlined the need for adding dextranase to the process in order to maintain the achievable 90% slicing capacity.

Apart from the dextran problem of frost-damaged beets, the processing of this beet material suffered severely from another deterioration quality parameter, which could be readily identified as the invert problem. Already from the analytical monitoring of the frost problem (see above) it turned out that in frost-damaged beet the invert sugar content is at least two times the normal level. The invert sugar is converted into organic acids by alkaline degradation in juice purification and so largely determines the alkalinity of the juices. As a consequence of the high

invert content of frost-damaged beets, a poor juice alkalinity is to be expected. Additionally, the lime salts content after purification will be high at low juice alkalinity. This phenomenon is analytically represented by the determination of the effective alkalinity (EA) of the first carbonatation juice: it gives the difference between the alkalinity of the first carbonatation juice and the expected lime salts content of second carbonation juice. In case the $EA < 0$, the produced thin juice will have a relative high lime salts content and will behave rather thermolabile (i.e. pH-drop) in evaporation as well. In Figure 7 the course of the EA is given, which clearly demonstrates the substantial change of the EA around the start of processing frost-damaged beets (i.e. ± 15 December). Despite the addition of large quantities of caustic soda to juice purification, we were not able to compensate for the excessive alkali consumption caused by the considerable invert sugar content of the processed beet. This is illustrated by an unchanged negative EA in the period that the frost-damaged beets were processed. The lime salts content of the second carbonatation juice also increased markedly, from $\pm 5\text{mg CaO}/100\text{ml}$ before 15 December to (on the average) $10\text{-}15\text{mg CaO}/100\text{ml}$ during the last week of the campaign. Finally, the high invert sugar content of the raw juice gave rise to a high thin juice colour as well: see Figure 8.

Last but not least: the thin juice purity dropped about 3 units due to the processing of frost-damaged beet; the thin juice purity by the processing of frozen beets amounted to 92, whereas the processing of frost-damaged beets resulted in a thin juice purity of 89.

Conclusions

The filtration problems caused by the processing of frost-damaged beets, as a result of the presence of dextran, can be almost completely solved by the addition of dextranase to the extraction system; upon dosage of 10ppm NOVO Dextranase 50L, the slicing capacity could be restored to 90% of the nominal capacity of the factory. The only requisite is a decrease of the juice temperature in the extraction system, in particular at the countercurrent-mixer/tower bottom side, in order to prevent a too fast deactivation of the dextranase enzyme. As a consequence, the diffusion efficiency will be slightly lower than normal.

It should be noted here that in the underlying research the raw juices were checked for microbial levan (polyfructose) as well, but it appeared to be absent in all samples.

The excessive invert sugar content of frost-damaged beets turned out to cause the major processing problem. It caused a considerable consumption of alkali, which necessitated the addition of a huge amount of caustic soda to juice purification, evaporation as well as crystallisation. Nevertheless, the lime salts content after second carbonatation increased substantially. Furthermore, the melassigenic nature of the (extra) invert sugar of frost-damaged beets made the molasses exhaustion troublesome, thus decreasing the yield of obtainable white sugar.

Finally, due to the high invert level, the juice/syrup colours increased markedly and, consequently, it became more difficult to produce white sugar according the required specification for colour.

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Figure 1. Example of sugar beet frozen at the top

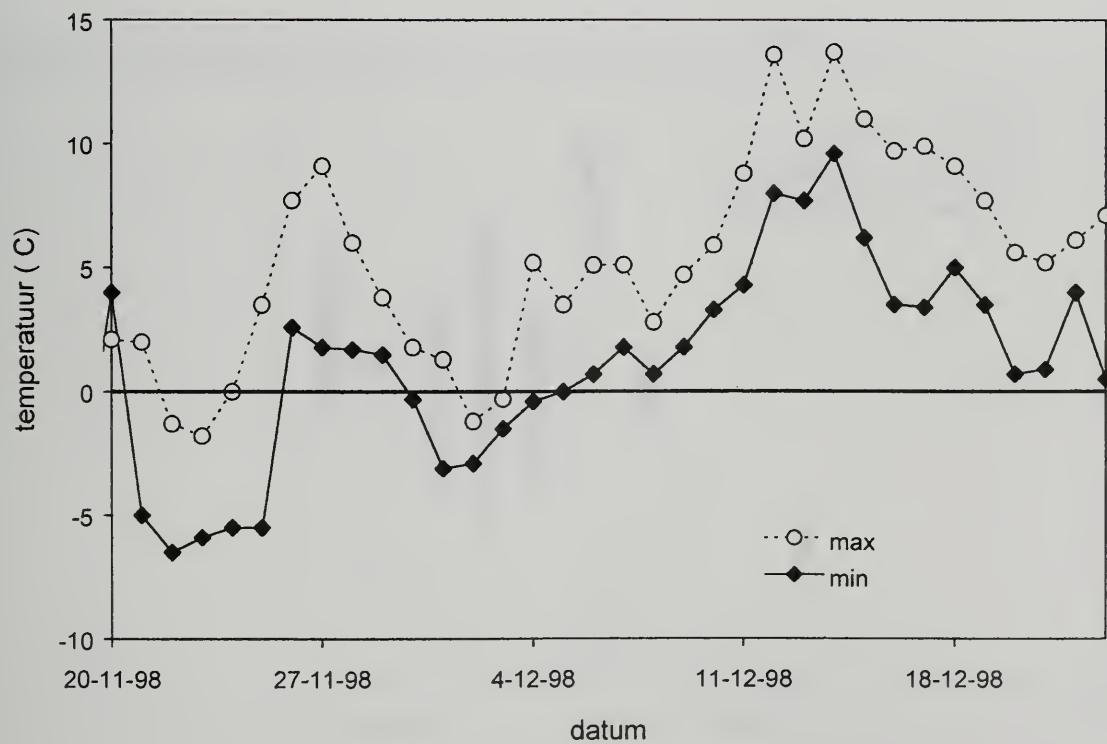


Figure 2. Outside temperature from mid-November to the end of the campaign in 1998

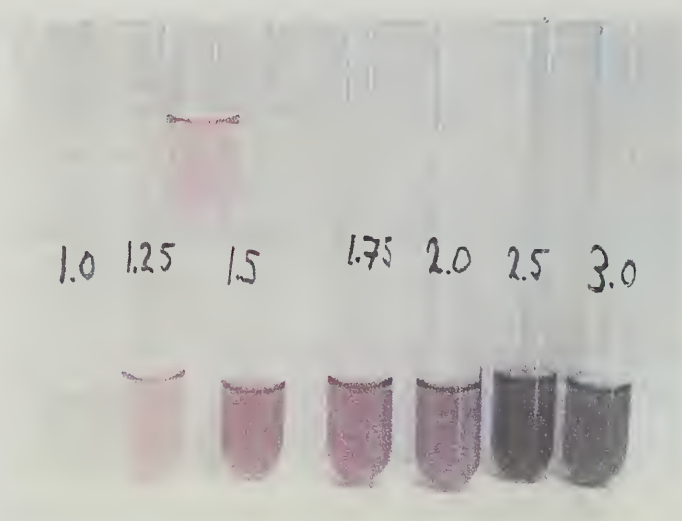


Figure 3. The rapid colorimetric test for invert sugar: visual comparison of an unknown sample with a series of invert standards.

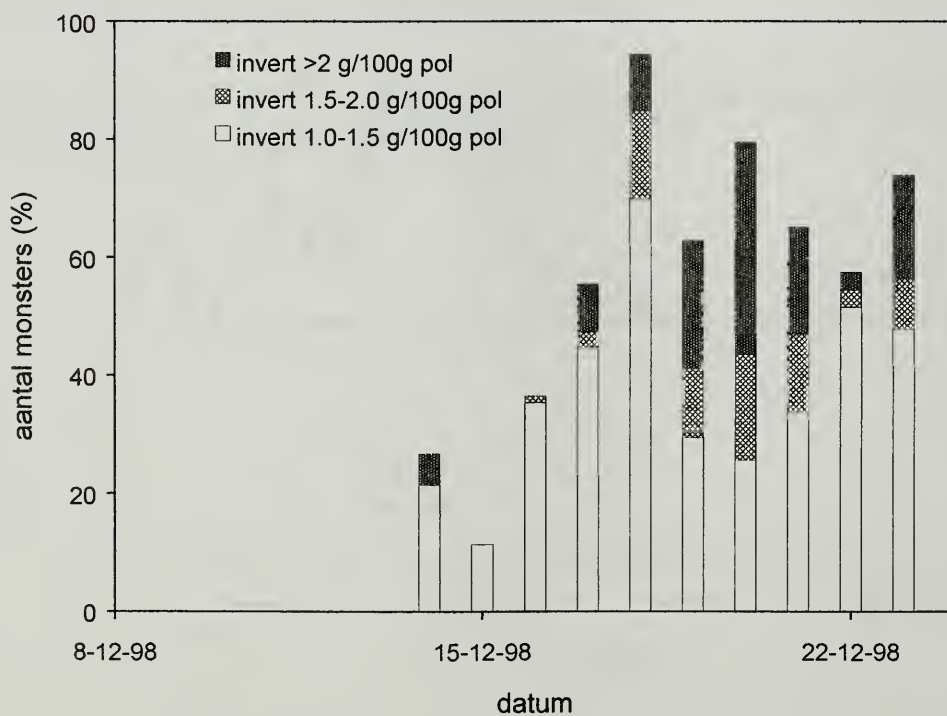


Figure 4. Indication of frost-damage by the rapid invert test.

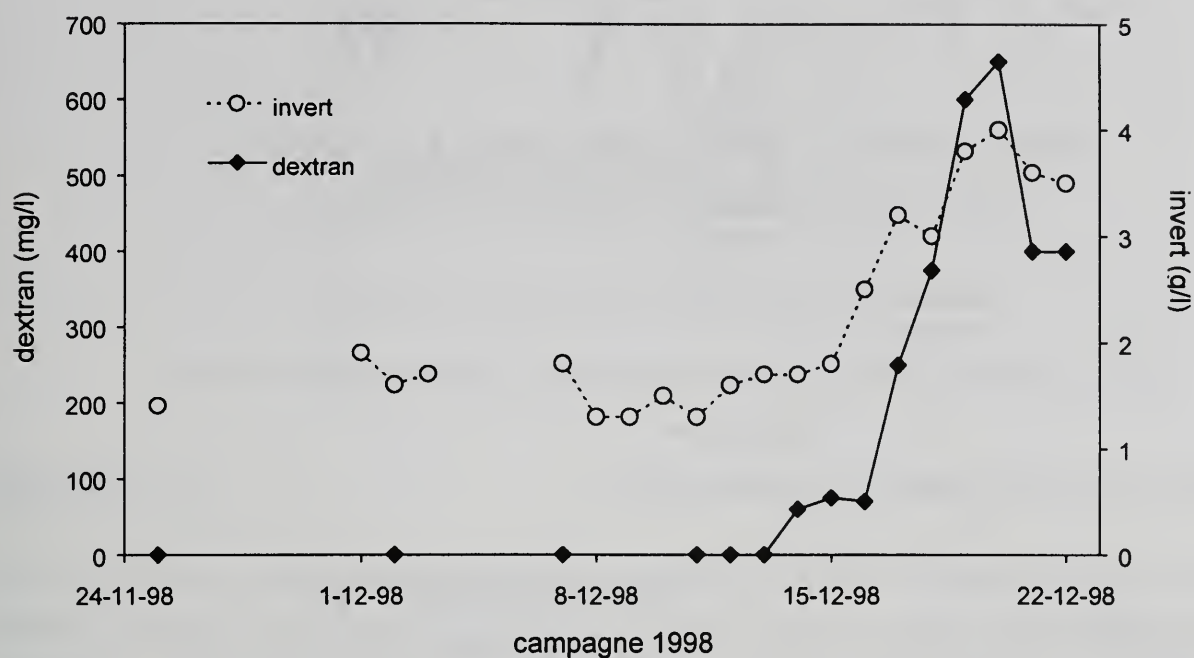


Figure 5. Invert sugar and dextran in raw juice from CSM factory 1.

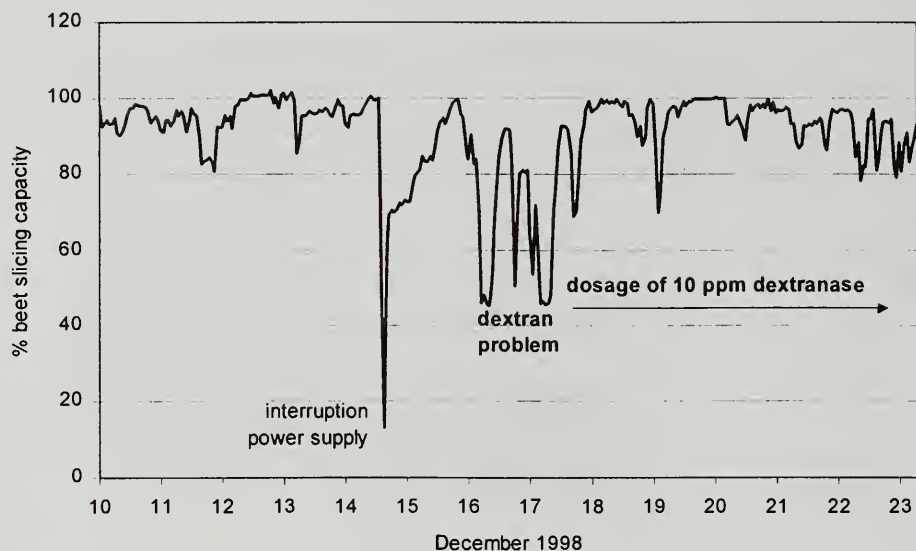


Figure 6. Slicing capacity of CSM factory 1

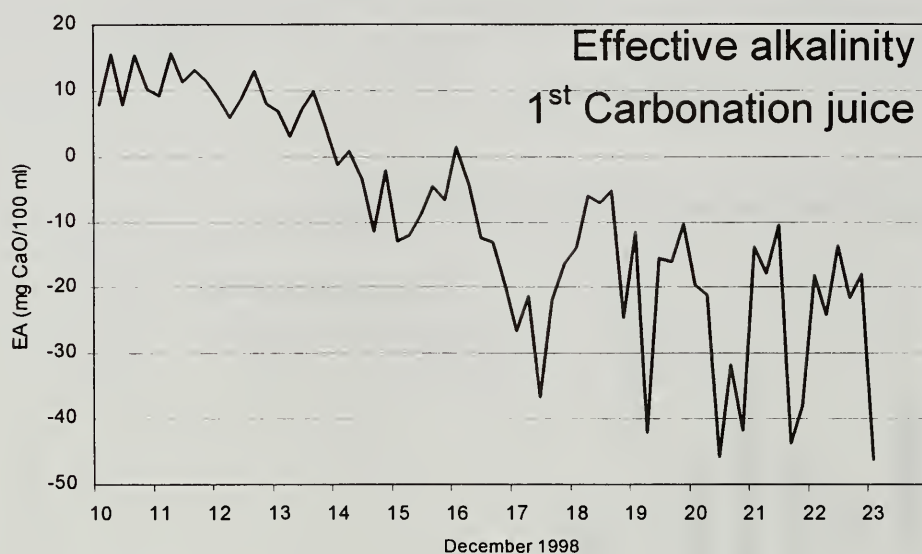


Figure 7. Course of the effective alkalinity (EA) of 1st carbonatation juice

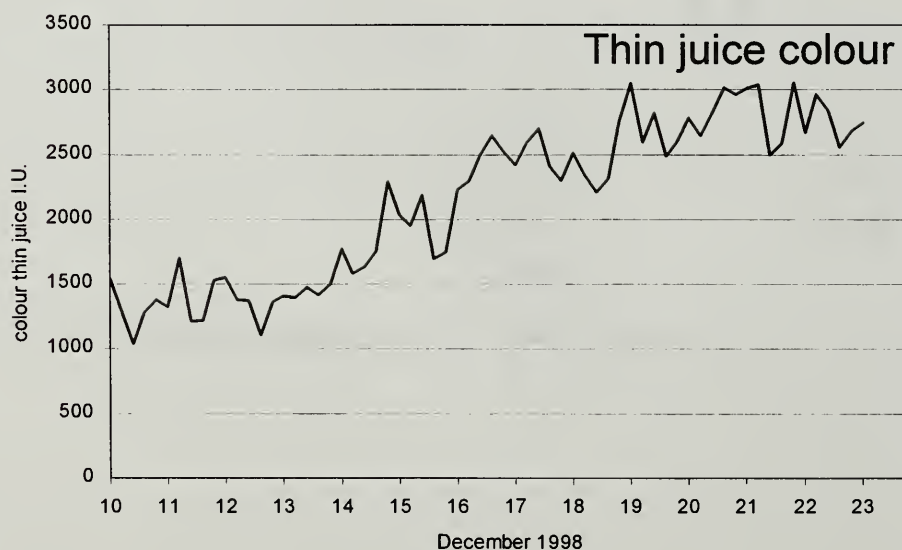


Figure 8. Course of the thin juice colour

GOOD LABORATORY PRACTICE AND LABORATORY CERTIFICATION

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ABSTRACT

How does a user of laboratory services know when he or she is receiving high quality testing services? Should the customer/client simply assume that the quality of laboratory services is adequate? Laboratories can be certified by a governmental agency or accredited by a professional organization, but is this enough to have confidence in the laboratory? Guidelines on good laboratory practice are available, and the laboratory should be able to demonstrate and document their procedures as well as to explain how the accuracy and reproducibility of methods was established. The American Chemical Society has developed 10 principles for good laboratory practice and these will be presented, along with discussions about proficiency testing and the guidelines that have been adopted for assessing the competence of testing laboratories.

An R&D laboratory should subscribe to the same quality criteria as a commercial laboratory because the results of research, when published in the literature, are used by others for further work. The credibility of an R&D lab depends on its adherence to demonstrated good laboratory practices.

INTRODUCTION

The importance of providing guidance to the sugar processing industry on the questions raised above is an ongoing concern. The sugar industries walk a tightrope in producing high quality and specialty products amid a maze of international regulations. Good laboratory practices (GLP) can be used as a balancing pole to negotiate that tightrope over regulations governing product development (6).

In this paper, the Principles of Good Laboratory Practice will be presented followed by discussions concerning laboratory certification/accreditation and proficiency testing.

Good Laboratory Practices

Good Laboratory Practice (GLP) is a quality system concerned with the organizational process and the conditions under which non-clinical health and environmental safety studies are planned, performed, monitored, recorded, archived, and reported.

The American Chemical Society (ACS), the world's largest scientific organization, has recently developed a set of laboratory policy guidelines entitled "Principles of Good Laboratory Practice" (1). These guidelines (see Appendix) were developed to assist the providers and users of laboratory test results by stating in simple terms the overriding principles that define the basic requirements of good laboratory practice.

The services provided by a laboratory can be thought of as conducted in a "total testing process," being made up of preanalytic, analytic, and postanalytic phases (2). The provider and the customer/client of laboratory services must recognize the importance to the "total testing process." Both play significant roles in reducing errors and ensuring the highest quality test results. Because of this, the ACS first principle stresses the need for close communication and collaboration between providers and customer/clients of laboratory services. In addition, the first principle also emphasizes the importance of locating a laboratory that possesses competent management and staff.

In essence, if a customer/client wants to ensure high quality laboratory services, then the customer/client should find a laboratory that closely follows the 10 principles of good laboratory practice put forth by the ACS policy.

Laboratory staff must be able to provide documentation establishing the accuracy and reproducibility of their analytical procedures. They should provide explanation of how the goals for allowable inaccuracy, nonreproducibility, and timeliness are met.

Customers/clients should evaluate the competence of the laboratory managerial staff by asking questions and viewing documentation about quality assurance, safety, and training practices. Continuous quality improvement (CQI) should be the overall objective of all laboratory practices, taking into account technological changes as well as existing guidelines and protocols. CQI also includes the good laboratory manager's commitment to training, retraining, and safety of the laboratory staff.

Documentation is essential throughout the "total testing process" to ensure that all quality assurance activities have taken place, including those addressing laboratory staff competence.

Laboratory Certification

Any analytical laboratory with a firmly established quality assurance/quality control (QA/QC) program may find laboratory certification/accreditation easily accomplished. The certification of laboratory means that some independent auditor has reviewed the laboratory staff, capabilities, and procedures against some set of requirements and standard practices and judged the laboratory and staff capable of routinely performing some kind of work while adhering to those requirements and practices.

A laboratory that claims GLP compliance can expect periodical audits from government agencies or professional organizations. In the case of EPA audits, one might expect an interim period of 15 – 24 months between audits (6). Laboratories can expect auditors to inspect facilities for cleanliness, security, and work place environment (i.e., size, air handling, temperature, and humidity). Auditors will interview laboratory personnel to establish their level of competency. Everyone should have the required knowledge, skills, and abilities to perform assigned tests, and everyone should be receiving adequate training and retraining.

Instrumentation is another area that laboratories can expect auditors to closely inspect. Are the right instruments available for doing this type of work? Are maintenance records in place and well kept? Are calibration practices and traceability of standards documented? These questions are just a sample of what the auditor will be looking to answer.

Standard operating procedures (SOPs) should be readily accessible for managers, analysts, and technicians alike. SOPs that should be available to all laboratory workers include: analytical methods, equipment operation, sample handling, and data storage. A written protocol should exist for almost every process in the laboratory.

Finally, laboratories themselves should administer audits to verify that good laboratory practices support their own data.

When testing issues apply to items in international trade, it is a tedious burden to retest the items after importation. This has caused a trend towards international laboratory certification/accreditation. The advantages of international laboratory certification/accreditation can be realized if one supposes that an imported product can be tested and certified to be of some quality in the exporting country to standards that are acceptable in another country. This eliminates the need for retesting items or wasting money importing items that may be rejected.

Proficiency Testing

Proficiency testing has been a serious topic within the sugar processing industry for some years now. At the 1994 ICUMSA meeting in Havana recommendations were made for process laboratories and process control methods (3). Roger Wood has pointed out that in recent years greater emphasis has been placed on the proficiency of a laboratory (4). Laboratory certification/accreditation and participation in proficiency testing is becoming very important.

The Institut für Technologie der Kohlenhydrate – Zuckerinstitut, Braunschweig, provides standard sugar with a certified color. The American Association of Cereal Chemists (AACC), the American Oil Chemists Society (AOAC – Smalley check sample program), and the Corn Refiners Association (CRA) have conducted check sample programs for several years for their industries. In the UK, the United Kingdom Food Analysis Performance Assessment Scheme (FAPAS), organized by the UK Ministry of Agriculture, Fisheries, and Food, has conducted analytical laboratories proficiency testing since 1990 by circulating a series of certified test materials to participating laboratories (5). All of these programs are self-supporting and charge a fee.

Improvement occurs in an analytical laboratory's ability with increased participation in proficiency testing in almost all areas of analysis (5), i.e. laboratories become more proficient and can perform self-checks to improve performance.

The 1998 ICUMSA meeting lists two guidelines for laboratory proficiency testing:

- (1) ISO Guide 43 (1984) Development and Operation of Laboratory Proficiency Testing, and
- (2) The International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories, Pure and Applied Chemistry, Vol. 65, 1993, pp. 2132-2144.

ISO 9000

The International Organization for Standardization (ISO) is a worldwide federation of national standards bodies from some 130 countries, one from each country. ISO is a non-governmental organization established in 1947. The mission of ISO is to promote the development of standardization and related activities in the world with a view to facilitating the international exchange of goods and services, and to developing cooperation in the spheres of intellectual, scientific, technological and economic activity. ISO's work results in international agreements that are published as International Standards.

ISO 9000 is rapidly becoming the most popular quality standard in the world. Thousands of organizations have already adopted this important standard, and many more are in the process of doing so. ISO 9000 applies to all types of organizations. It doesn't matter what size they are or what they do. It can help both product and service oriented organizations achieve standards of quality that are recognized and respected throughout the world.

ISO 9000 can be readily integrated into your organization. For instance, you decide that you need to develop a quality system that meets the ISO 9000 standards. You choose to follow this path because you feel the need to control the quality of your products and services, to reduce the costs associated with poor quality, or to become more competitive. Or, you choose this path simply because your customers expect you to do so or because a regulatory body has made it mandatory.

You then develop a quality system that meets the quality requirements specified by one of the following three standards: ISO 9001, ISO 9002, or ISO 9003. In the course of doing so, you also consider ISO's many guidelines. These guidelines include ISO 9000, ISO 9004, ISO 10011, and ISO 10013. Once your quality system has been developed and implemented, you carry out an internal audit to make sure your system is working properly. Then you invite an accredited external auditor (registrar) to evaluate the effectiveness of your quality system. If your auditors like what they see, they will certify that your quality system has met all of ISO's requirements. They will then issue an official certificate to you and they will record your achievement in their registry. You can then announce to the world that the quality of your products and services is managed, controlled, and assured by a registered ISO 9000 quality system.

CONCLUSIONS

Customers/clients want to get what they pay for; however, the customer/client must be aware that the testing operation often requires direct participation from them. For example, sample contamination by the customer/client cannot be corrected by the laboratory. Also one must realize that the quality of laboratory services cannot automatically be assumed to be adequate. Neither is the presentation of a certificate from a government agency or a professional organization assurance of high quality test results. The customers/clients must assess the laboratory for themselves based on the principles of good laboratory practices.

Adherence to the “10 Principles of Good Laboratory Practice” provided by the American Chemical Society by both providers and customers/clients of laboratory services will help to ensure high quality testing.

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APPENDIX

PRINCIPLES OF GOOD LABORATORY PRACTICE FOR CHEMISTS WHO PROVIDE LABORATORY SERVICES AND THEIR CLIENTS

INTRODUCTION

These principles were developed to state in simple terms the overriding guidance behind all of the highly technical laboratory standard and guideline documents that have been created by professional organizations over the years. These principles are intended to assist both the providers and users of laboratory services by defining in a straightforward way the basic requirements for good laboratory practice.

PRINCIPLES

1. Good laboratory practice requires close communication and collaboration between clients, managers, and knowledgeable laboratory staff throughout the "Total Testing Process."*
2. The management system used should permit the appropriate selection of laboratory tests, with timely and reliable test performance, consistent with established goals for quality, accessibility, and cost.
3. Everyone involved in the "Total Testing Process" should have the required knowledge, skills, and abilities to properly perform his/her assigned tasks.
4. The risk-prone steps in the "Total Testing Process" should be identified and monitored continuously in order to prevent or minimize the adverse consequences of mistakes.
5. The accuracy of the analytic portion of the "Total Testing Process" should be established before testing is initiated and should be periodically assessed thereafter.
6. The reproducibility of the analytic portion of the "Total Testing Process" should be established before testing is initiated and should be monitored using quality control programs designed to evaluate the entire analytic procedure.
7. Goals for allowable inaccuracy, nonreproducibility, and timeliness of results should be consistent with management and client needs and with the state-of-the-practice.
8. It is the responsibility of everyone to maintain a safe environment for clients and staff.
9. Documentation is an essential process to ensure that all quality assurance activities have taken place, including those which periodically assess staff competency.
10. Continuous quality improvement (CQI) should be the overall objective of all laboratory practices taking into account such factors as cost-effectiveness, the development of new tests and technologies, deletion of obsolete tests, and staff training and retraining.

* The "Total Testing Process" consists of: the selection of appropriate tests or measurements to address the scientific question; proper preparation and collection, handling, and storage of samples; application of appropriate techniques and methods in performance of the test; timely and accurate reporting of the test results; and accurate interpretation of results with application to the question.



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PROGRESS IN IMPROVING THE STANDARDS OF ANALYSES IN FACTORY LABORATORIES

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Abstract

The laboratories of the Sugar Milling Research Institute (SMRI) have the responsibility of maintaining and improving the standards of analytical work within the SMRI itself and throughout the South African sugar industry. This is achieved through the following:

Interlaboratory work, involving check samples and ring tests. An award is presented annually to the best factory laboratory.

Audits of the laboratories at the sugar factories.

Training of factory laboratory staff.

Evaluating laboratory equipment and consumables with the aim of recommending them for use in the industry.

Method development, evaluation and collaborative studies involving the International Commission for Uniform Methods of Sugar Analyses (ICUMSA).

The paper describes how the above is carried out and comments on the progress that has been made in the South African Industry.

Introduction

The Analytical, Chemistry and Biotechnology laboratories at the Sugar Milling Research Institute (SMRI) provide routine services for the South African Industry, its members (Swaziland) and affiliate members (Malawi, Zimbabwe, and Zambia), in addition to being centres of research. The laboratories were accredited in 1999 by the South African Accreditation Services (SANAS) and are recognised throughout the region and internationally for the delivery of analytical services of the highest standard. All calibrations are traceable to international standards and all accredited methods are validated. The SMRI laboratories communicate with the seventeen mill laboratories as well as the Cane Testing Services (CTS) laboratories, the South African Sugar Terminals (SAST) laboratory and the Tongaat-Hulett Central Refinery (HULREF) and Technical Services Division (STD) laboratories

Through participation in ring tests the SMRI is also in contact with overseas laboratories. This effective communication assists in maintaining a high level of analytical control in the factories.

Interlaboratory work

Samples of very high pol $>99,3^{\circ}\text{Z}$ (VHP) sugar are distributed to the mills on a weekly basis and analysed for pol, moisture and colour. The four central laboratories SAST, STD, HULREF and SMRI also analyse these samples and the average is used as a control for comparison with the mills. This information is compiled into a monthly interlaboratory report and a VHP check sample report, and distributed to the mills. Figure 1 shows the colour comparisons for the four control laboratories. Figure 2 shows the comparison between the control value and the mill value for the pol parameter.

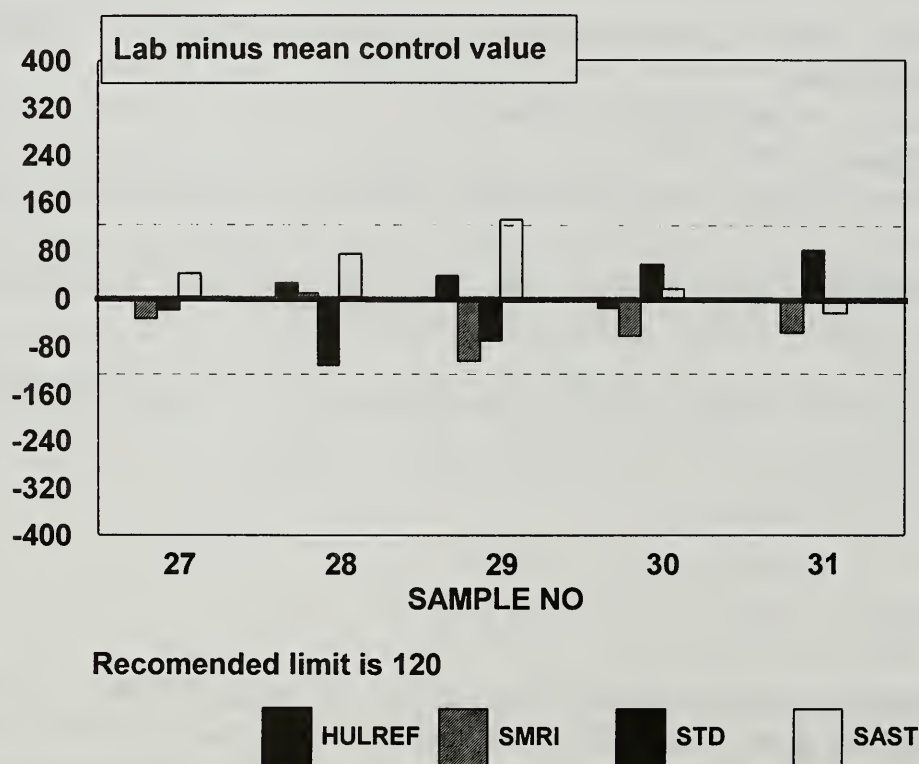


Figure 1. Control laboratory comparisons for VHP colour

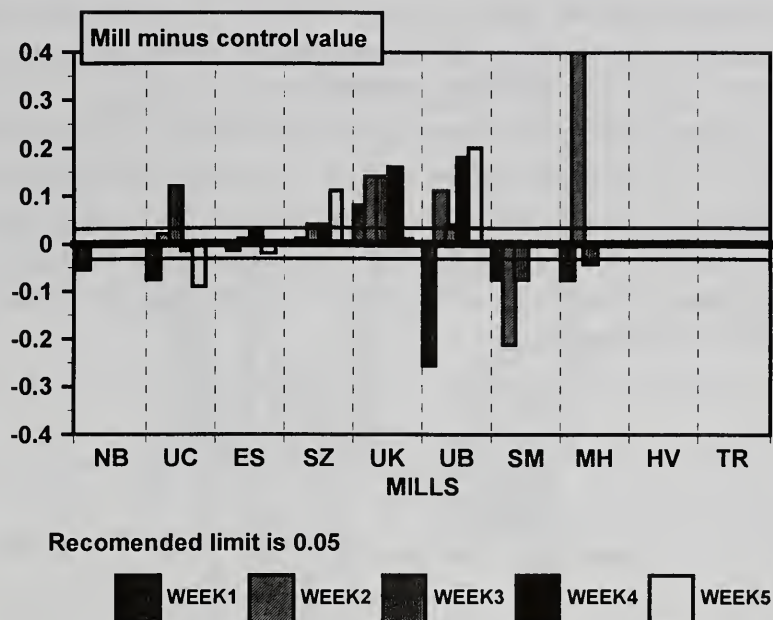


Figure 2. Mill versus control comparisons for VHP pol

Similarly, refined sugar check samples analysed by the SMRI are sent to the five mill laboratories servicing back end refineries every week. The analyses performed are pol, moisture, colour, turbidity, residual sulphur dioxide, conductivity ash and grain size. This information together with the microbiological analyses are specifically requested by the bottling companies and appears on a certificate of analysis. Figure 3 shows the refined sugar check sample colour comparisons.

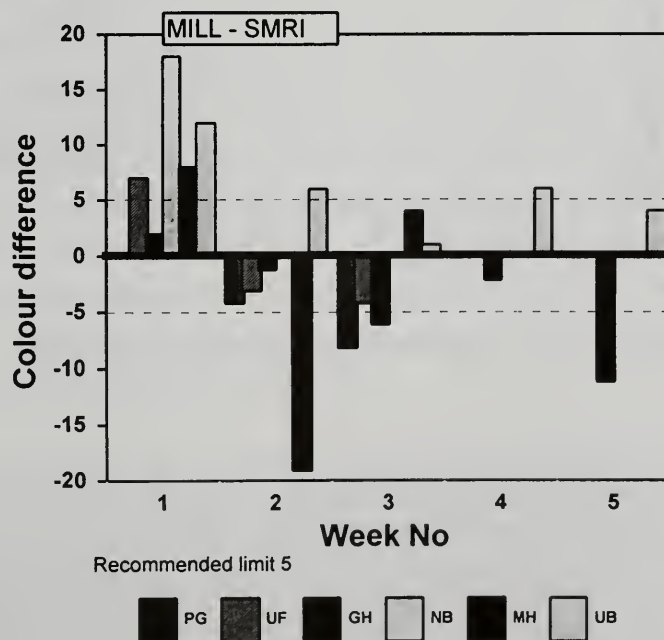


Figure 3. Mill Versus SMRI Comparisons for Refined Sugar Colour Analysis

One of the driving forces behind the accreditation of the SMRI laboratories was the generation of results for cane payment purposes based on the analysis of mixed juice. As the accredited tests which are performed are subject to external audit by SANAS there could be no perception of bias in favour of either miller or grower. Samples representing the weekly crush are frozen, packed in insulated containers and sent to the SMRI where they are composited and analysed for pol, brix and sucrose. The pol and brix results are compared with those from the mills and the comparisons distributed to the regional chemists of the CTS. Differences greater than 0,05 on each parameter are considered unacceptable and would trigger an investigation by the CTS chemist. Figure 4 shows a typical bar graph of these comparisons during the course of the season. This information is useful in highlighting problems which may occur as a result of analytical errors, errors in sampling procedure, and variation in operation and performance of instrumentation.

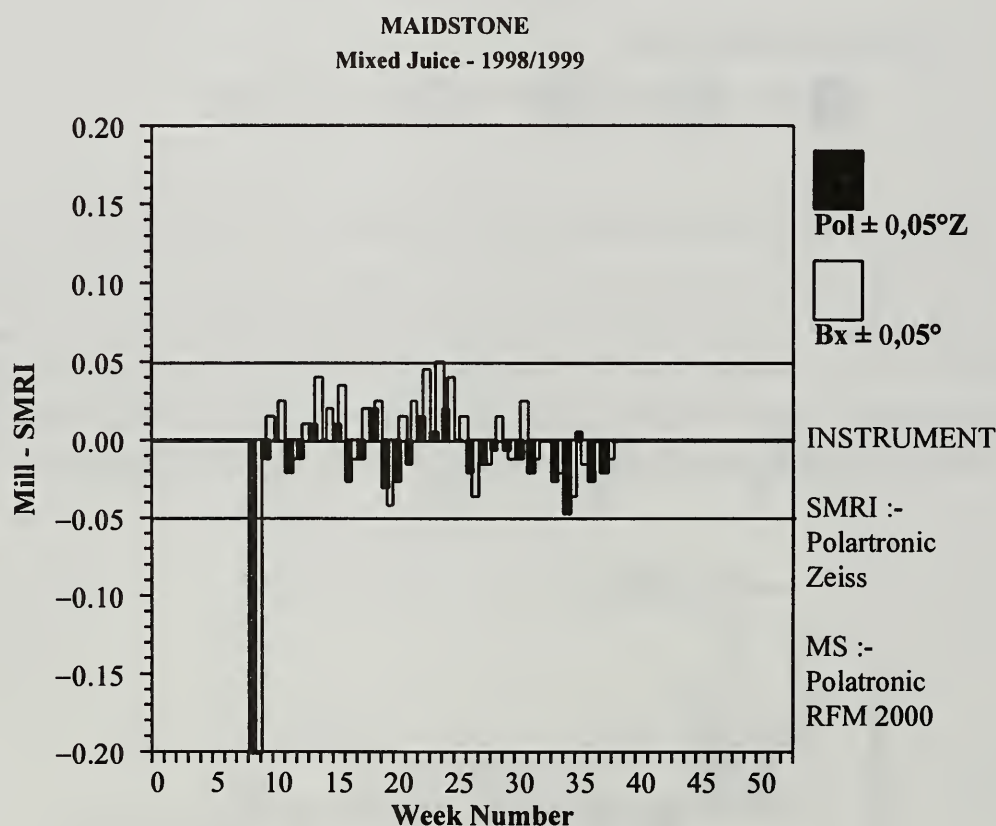


Figure 4. Bar Graph showing mill versus SMRI comparison for mixed juice analysis.

Pol and brix analyses of final molasses are used by the factories for mass balances and recovery calculations. Final molasses composite samples are sent to the SMRI on a weekly basis for a target purity difference (TPD) analysis. TPD is a measure of exhaustion of final molasses. Analyses include pol, brix, sulphated ash, dry solids and gas chromatographic (GC) fructose, glucose and sucrose. Each factory also determines the pol and brix of the composites. Certain tolerances have been established for the reproducibility of pol and brix analyses (Mellet *et al* 1982) and it is obvious from the bar graph (Figure 5) whether a particular laboratory is within tolerance. The data prompts the laboratory staff to take corrective action, when necessary.

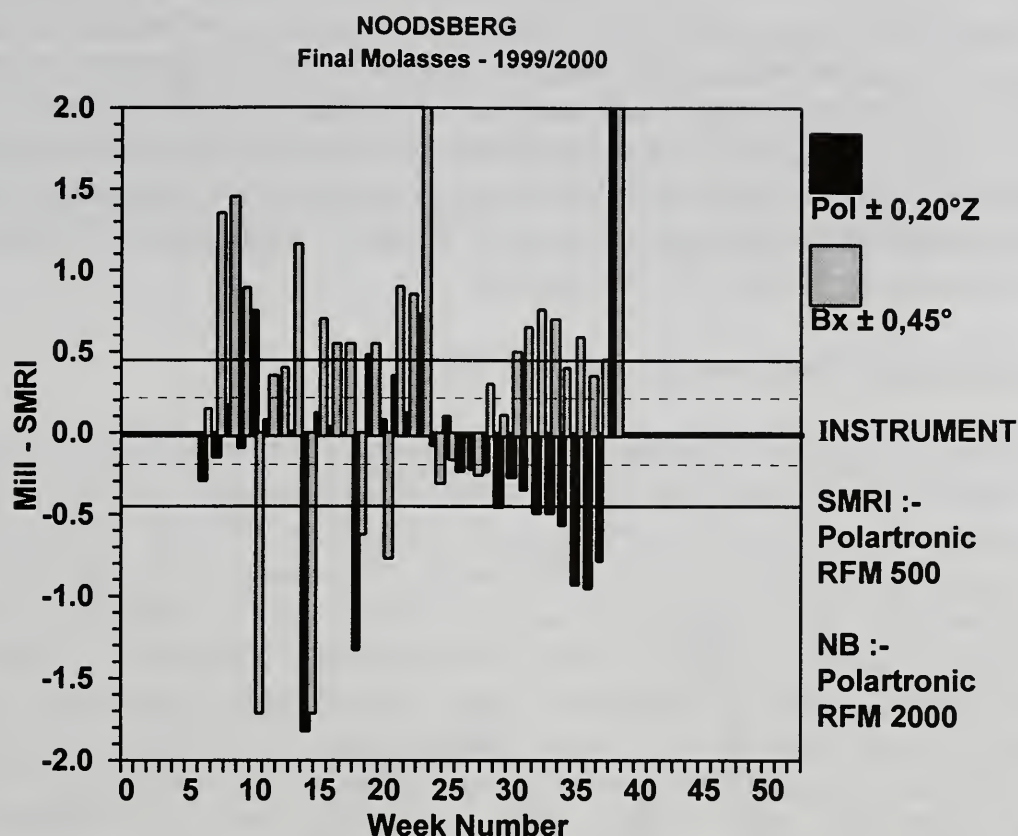


Figure 5. Bar graph showing mill versus SMRI comparisons for final molasses.

As an incentive to the mill laboratory staff to maintain a high level of analytical work a trophy, “The Best Laboratory Award” is presented annually. Two mills have won this award on three consecutive occasions since its inauguration six years ago. It is interesting to note that these two mills have been proactive in monitoring the data from the interlaboratory comparisons and engaging in effective corrective action in consultation with the SMRI. The data from the VHP check sample and molasses comparisons is used to calculate a percentage of analyses which are within tolerance. The trophy is given to the mill with the highest percentage of analytical results within tolerance.

Audits at sugar factory laboratories

The SMRI offers comprehensive audits of mill laboratory equipment and procedures. Instrumentation calibration includes refractometers, polarimeters, pH meters, spectrophotometers, balances and ovens. Included in the audit are sampling and operational procedures for the direct analysis of cane (DAC) and all intermediate products used for cane payment or factory control purposes. It is noticeable that where the mills have recognised discrepancies from the interlaboratory comparisons and requested an audit there has been marked improvement in agreement with SMRI analytical results following the audit on corrective actions.

Training of Factory staff

The audits tend to highlight problem areas in analytical procedure at the mill laboratories and this information is fed back to the training officer who runs the Laboratory Workers Course at the Industrial Training Centre (ITC) based in Mount Edgecombe. The course consists of three modules and provides the analyst with training in basic analytical technique through to calculations required for factory performance evaluation. The training officer is backed up by the expertise of laboratory staff at the SMRI laboratories. The SMRI also provides specialist on site training when this is more convenient. For example gas chromatographic analysis. In addition training in the SMRI laboratories is facilitated when requested by the mill management.

Instrumentation and Consumable Evaluation

Attempts to standardise on analytical instrumentation to eliminate instrument bias have largely been successful as a result of agreement of the SMRI to evaluate instrumentation prior to installation in the mill laboratories. Until recently instrumentation supplied by different manufacturers was responsible for significant differences in analytical results. For example, investigations by Mellet (1991) revealed that five different makes of refractometer were in use at that time. They included the Schmidt and Haensch Refractomat (Refractomat), the Schmidt and Haensch DUR (DUR) and the Bellingham and Stanley RFM 80, 81 and 2000. It was found that the Refractomat gave lower brix readings on dark coloured solutions (A, B and C molasses, nutsch molasses, massecoites). The magnitude of the difference varied from sample to sample but on average was found to be $\text{RFM 2000} - \text{Refractomat} = 0.48$, $\text{RFM 2000} - \text{DUR} = 0.21$. The industry has now standardised on the Bellingham and Stanley refractometer, either the RFM 2000 or the RFM 510. The Schmidt & Haensch Polartronic has also been standardised throughout the South African Sugar Industry. As mentioned previously the refractometers and polarimeters are supplied by single manufacturers. Other instruments such as pH meters, conductivity meters and spectrophotometers used for routine analyses are evaluated and the appropriate recommendations made.

Recent investigations into discrepancies in colour comparisons between the SMRI and mill laboratories revealed in most cases the incorrect choice of pH electrode for pH measurement of sugar solutions. Consultation with electrode manufacturers and evaluation of their electrodes has been fruitful and a recommendation to standardise on a particular electrode will be made shortly. Considered equally important is the evaluation of consumables (chemical reagents and laboratory supplies). For example filter paper used for pol and brix analysis are subject to tender. Prior to purchase they will be evaluated against existing filter papers. This approach assists mills in running cost effective laboratories without compromising analytical standards.

Method Development and Evaluation

Ongoing research is conducted in this area with a view to providing mill laboratories with rapid up to date analytical methods which are cost effective. The SMRI communicates with international bodies such as the International Commission for Uniform Methods of Sugar Analysis (ICUMSA). Through participation in ring testing with international laboratories the SMRI laboratories are able to benchmark their capabilities. Methods developed in house are validated in accordance with

requirements stipulated by the accreditation body, SANAS which has international recognition through Mutual Recognition Agreements (MRA's).

Promising results have been obtained in evaluating a new development has occurred in a clarifying agent (NCA) as an alternative to lead acetate. Long wavelength polarimetry (LWP) has also shown potential and could preclude to use of lead in plo analysis. Figure 6 shows the comparisons for pol at one of the mills using the alternative clarifying agent and long wavelength polarimetry and conventional procedures using lead acetate as the clarifying agent. The pol analyses are also compared against the true (GC) sucrose. This topic will be the subject of future publications.

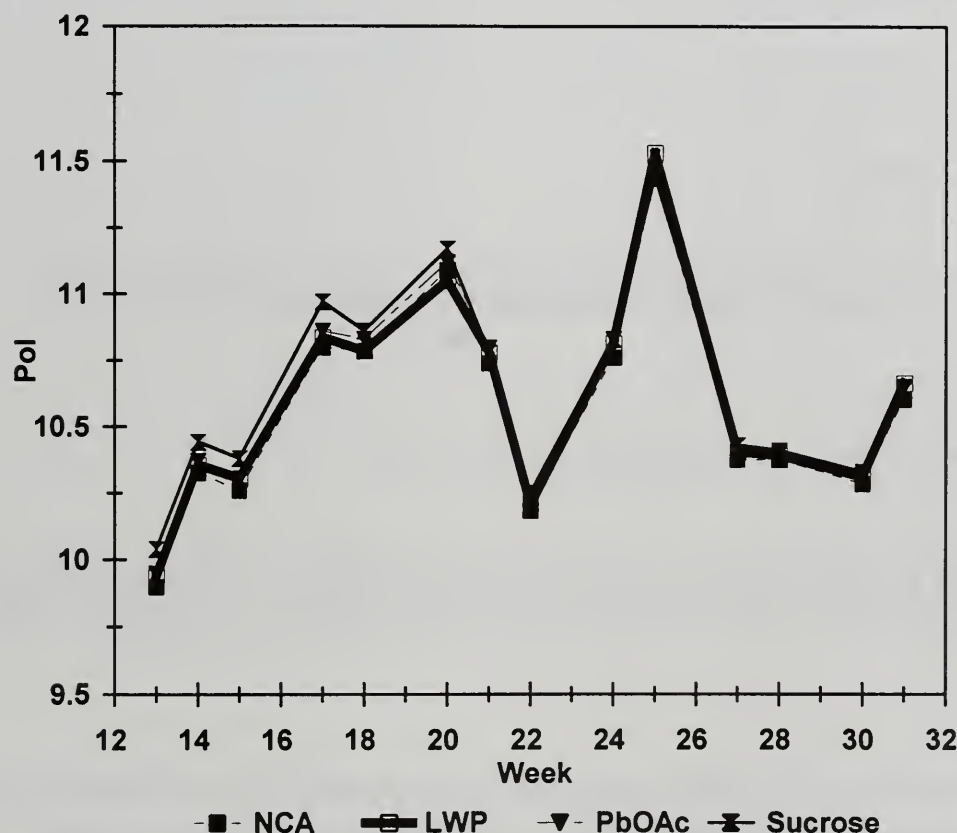


Figure 6. Pol comparisons using new clarifying agent (NCA), lead acetate and long wavelength polarimetry.

Sulphated ash (SA) measurements used for the calculation of TPD figures have been replaced with conductivity ash (CA) measurement and this is to be implemented for the 2000/2001 season. The latter is a much quicker method and does away with the environmental problems associated with sulphated ash analyses. The sulphated ash and conductivity ash was measured for the 1999/2000 season and the effect on TPD calculated. Figure 7 shows the average target purity difference for each of the South African mills using the two different ash methods.

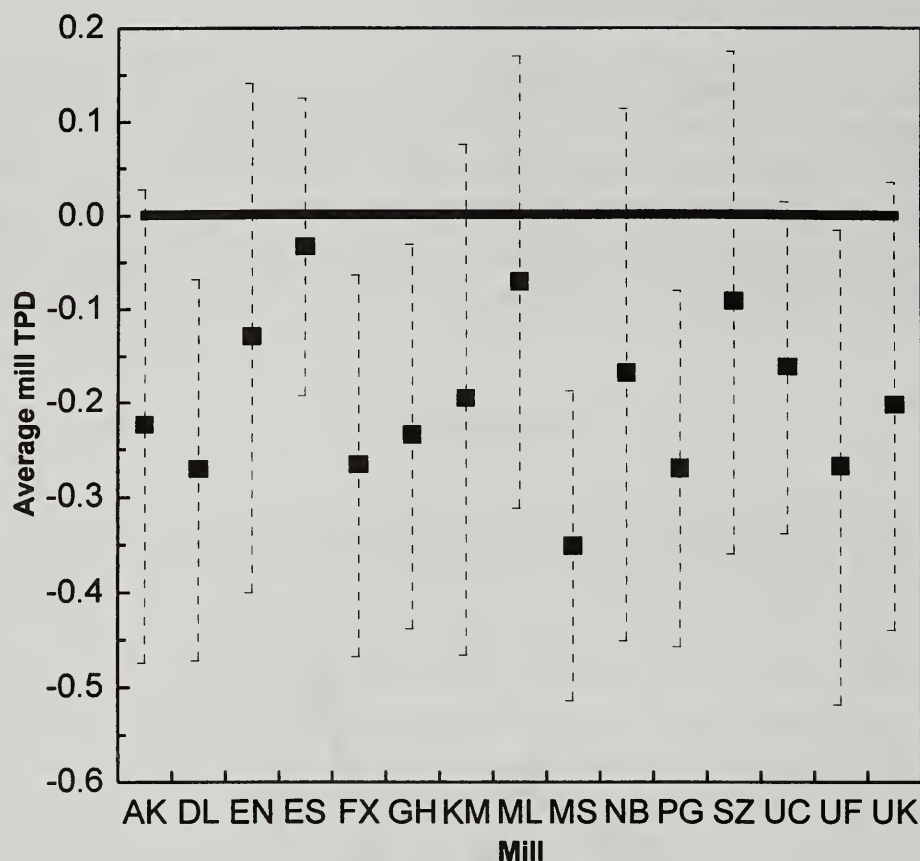


Figure 7. Average discrepancy in Mill TPD (CA - SA)

The measurement of refined sugar moisture by the Karl Fischer method is being investigated in consultation with ICUMSA and it is hoped that this will progress to become an official procedure.

Conclusion

Through the commitment of the SMRI laboratories to maintain a high level of analytical standard and effective communication/collaboration with the mill laboratories, the South African Sugar Industry has made considerable progress over the years in establishing a level of factory analytical control which is world class. The rigorously tested and documented procedures for sampling at the mill, mill laboratory analysis and comparison with SMRI analyses through to communication of data, give the industry confidence that it receives the appropriate and accurate information necessary for efficient sugar production.

Acknowledgments

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SUGAR PROCESSING RESEARCH AND DEVELOPMENT WITHIN BRITISH SUGAR

Ian Tebble and Dave Sargent

British Sugar

1. INTRODUCTION

This paper discusses the changes in the organisation of Research and Development within British Sugar in order to try and meet the challenges facing the company in the future.

The need for R&D is both to help the company protect its existing profitability in the face of external pressures and to enable it to exploit areas of potential opportunity.

There are 3 main areas that can effect the profitability of the company either as threats or potential opportunities.

1.1 Markets

Customers are always demanding improvements in quality and tighter product consistency. Additionally sugar is a commodity product and price is a major consideration for customers. There is pressure to reduce processing costs to maintain margins under increasing pressure on price.

1.2 Cost base

The cost of the raw material, beet is largely outside our control. However the other operating costs can be looked at. Reduction in fuel costs are a major potential saving together with reduced labour costs due to increased automation of plant. The cost of processing aids, including lime, can be reduced by better sourcing, using less or by changing to other materials. There is also the potential to change the traditional processes thus reducing operating costs and reduce the reliance on, or eliminate the use of, processing aids.

1.3 Regulatory framework

The effect of the quota system is to increase the pressure on reducing production costs to maintain profit levels. Emissions are also a major concern where investments may be needed to meet future legislation.

2. TARGETS OF R&D

From the effects of these external drivers three main target areas for research can be identified.

1. Production of lower cost sugar
2. Product differentiation
3. Interaction with the environment

Research can be focused into one of these areas but often will have impact across all areas.

2.1. Production of lower cost sugar

Other than reducing the cost of the raw material, beet, there are three possible approaches to achieving this goal.

- Improvements to existing process
- Use of alternative processes
- Manufacture of additional products/more effective use of by-products

Possible improvements to the existing process include reduced lime usage or increased energy efficiency as have already been carried out at many factories, or greater automation reducing labour costs. There can also be considerable savings made through better control of the process, reducing sugar losses etc.

There is the potential to use different technologies to transform and thereby cheapen, all or parts of the sugar process.

Having efficiently extracted the sugar there is the opportunity to utilise the residual materials in the most profitable way, in effect subsidising the cost of sugar production. The development of alternative products from beet pulp, molasses and lime should be considered. Also the use of existing plant to process alternative materials, for example out of campaign, must be considered.

2.2. Product differentiation.

Fundamentally this is a means to establish sugar products as speciality products rather than as commodities and hence maintain profit margins. The idea of added value to the customer is the main concept here. The main areas that can be addressed are quality and product development together with improved service and customer lock in.

The customer requires quality assurance through all parts of the process and needs effective auditing procedures to support it. A major product quality issue is particle size and consistency. Improvements in production technology are needed to give better control of the product in these areas. Also the organoleptic properties of the sugar are becoming increasingly important to customers. Improvements to the quality of the product help to add value to the product. There is also demand from some customers for a more natural product, loosely termed "organic sugar" which would require segregation from the conventional product.

There is considerable scope in carrying out research for customers. Working together to develop new product opportunities or modify the properties of existing products to improve their performance in customers products.

2.3. Interaction with the environment

Looking at the interactions of the sugar factory with the environment there is technology available to cope with most issues, at quite high cost in some cases although standards change rapidly and development is always needed. The impending tax on carbon dioxide emissions will be a challenge focusing attention on energy reduction. Eliminating ammonia emissions to atmosphere is also a potential area of research. Emissions to water are of considerable interest and quality standards for allowed discharge are becoming more difficult to meet. The beet sugar factory also relies on natural resources in the form of limestone and this is already an issue in the UK and elsewhere either with supply or disposal, driving research into lime free processes.

3. WAYS OF WORKING

There are at least four different approaches that can be used as part of the research plan to develop new technologies

- Wait and see
- Sponsored research
- Dedicated research
- Collaborative research

The first wait and see approach has the advantage that no specific R&D investment is required all that is needed is to wait until new technology is developed and proven and then purchase from an equipment supplier, sometimes involving a royalty payment, and install with minimal risk. However we still need the insight to recognise such developments and the potential benefits for our process. This approach should not just be limited to the sugar industry as solutions from other industries may well be applicable such as the introduction of gas turbine combined heat and power generators. The main downside to this approach is that the speed of development is outside your control

Sponsored research can be carried out at an academic institution such as a University or possibly a specialist research organisation. Such research can bring specialist knowledge to a particular

issue but there are problems. The timescales involved with Universities sometimes do not match the needs of the company and there is the requirement for publication of results, which is often not the intention of the company. With specialist research organisations there is the profit element to accommodate leading to the minimum work required to meet the contract and initial briefing and often no attempt will be made to follow up interesting leads or alter the planned work without some form of financial renegotiation

The advantages of a dedicated research program are that some form of commercial advantage may be attainable, the project timetable is controllable and there is a significant internal knowledge base built within the company. The major disadvantage is that there can be a considerable risk of failure or that the initial rewards of success can be much less than the expenditure requiring long payback periods.

Collaborative research can be an effective way to undertake a research program that would be beyond the financial and technical resources of any one member. Supply companies can also usefully be part of the group if they are willing to contribute in a realistic way. An element of control is possible but a lot of trust is required to make it work.

Within British Sugar we are using all of these approaches but find that we are making increasing use of collaboration programmes and sponsorship and expect to continue in this manner

4. RESEARCH AND DEVELOPMENT IN BRITISH SUGAR

Over the past few years there has been a change of emphasis in research from process related issues towards customer and product related projects and a corresponding reduction in the number of people involved in process projects. Ten years ago almost all the research and development was directed towards sugar processing whilst today less than 30% of staff are involved in process related research work. In order to best meet the needs of the company in terms of R&D and scientific support for sugar production the remaining process related science resource has been organised into one department, Operation Services Science (OSS), which is split into 3 teams. These are:

- Frontline team
- Support team
- New opportunities team

With the reductions in staff at factories over the last 10 years there was a corresponding reduction in scientific understanding of the process and the frontline team helps to overcome this problem. Each team member is primarily responsible for two factories and is seen as part of the factory team providing a main contact for further technical support when needed. The teams main role is in process troubleshooting, providing a rapid response to problems at particular factories, as well as looking at issues common to all sites such as optimising extraction. Importantly this team has a once weekly contact with the director of production. The team members have varied experience of process operation and considerable expertise and knowledge of specific areas of the process.

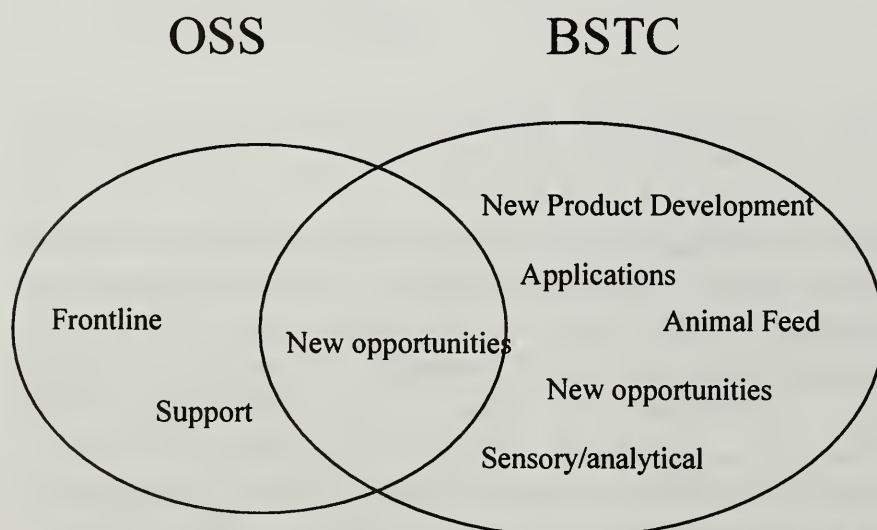
The Support team provide some routine analytical support that cannot be done at individual factories, including microbiological testing and trace metal analysis, together with instrument support for the factory laboratories. The team are also involved in a lot of project work , generally in the short to medium term, . Recent examples include reduction in acid insoluble ash levels in animal feed to meet changes in EU regulations, monitoring of pulp drier emissions, and also optimisation of sugar end purity profiles. The team are also involved in product quality and dealing with customer complaints.

The new opportunities team was set up to look at longer term projects. At present the major focus of this group is on further reducing lime usage, looking at the potential for lime reburning, as currently used at some factories in the US, as well as considering the potential for alternative processes such as the raw juice crystallisation process as suggested by Mantovani and Vaccari or the raw juice separation process proposed by Amalgamated Research Inc. An important role of this team is developing an understanding of technologies that may have future applications within the sugar industry such as membrane filtration and chromatography.

The organisation of these teams is fairly flexible so that people can be moved round to match skills with project needs. Currently about 50% of the people are involved in the support team with the remainder equally divided between the frontline and new opportunities teams. Additional temporary staff are also employed when needed, particularly during the campaign. All of the teams also work very closely with the engineering department to provide cross-functional teams for many projects.

The Frontline team and support team are based at the Wisington factory giving closer links to production, whilst the new opportunities team is based at the British Sugar Technical Centre, one step removed from day to day factory problems and allowing more focus on the longer term projects. This also allows interaction with the other research teams based at BSTC supporting various units within the British Sugar group outside of sugar production.

Organisation of Science Resource within British Sugar



There has been a change in emphasis in the work done at BSTC from largely process based to more product based with the building of a specialised food centre and the recruitment of food scientists and food technologists. The work carried out in the food centre can be divided into new product development and product applications together with supporting facilities such as analytical testing, sensory analysis (testing the organoleptic properties of products) and storage testing of products.

New product development

Development of sugar products to produce higher value products with increased product differentiation. Examples of these include Silk Icing – a new icing sugar product, and Half Spoon - an artificial sweetener and sugar mix.

Product applications

There is a team of food technologists providing information to customers on the best use of both sucrose and glucose products in their processes such as confectionery and bakery. This also includes carrying out research work for customers to develop their products.

In addition to the teams already mentioned, there are other teams looking at the development of opportunities away from the core sugar business and there is also support for the animal feed business.

There is also considerable amount of work carried out in conjunction with other research establishments and Universities. We are keen to expand on this further and look at ways to work with other companies and equipment manufacturers in the future. A recent change in emphasis of the direction of research has been to go out and look into other areas outside of British Sugar to find other uses for the expertise we have developed. This can be doing research work for our customers as part of the services we offer or potentially carrying out research work on a contract basis. This can generate extra funding to help support other internal research and also widens our scope of work potentially leading to other opportunities.

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THE NATURE OF COLORANT

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Introduction

Much is known about the nature of cane and beet sugar colorant, but in recent years, the thinking about colorant has shifted. The goal of sugar refining has always been to remove color. The goal of much research on colorant has been to characterize color fully and to understand its nature. However, it is also noted that color, *per se*, is not the only criterion for occlusion (transfer) of color into crystals, as shown by observations that a beet standard liquor (thick juice) of 2000-3000 ICUMSA color can produce a 20-30 white sugar; while cane final syrup color must be in the range of only 200-300 to produce a white sugar of a similar quality.

Obviously, the color of most interest is that which transfers into the crystal; color that does not transfer into crystal can be washed off during centrifugation, and is of less interest.

This paper examines some factors in cane and beet sugar colorant that affect transfer of color into the sugar crystal, including studies that show the influence of turbidity, polysaccharides, and high molecular weight content. The nature of various colorants using fluorescent profiles will be demonstrated.

Color Types

Sugar color is not one single molecular entity, but rather a wide range of materials, each with its own characteristics of molecular weight, pH sensitivity, charge, chemical composition, and affinity for the sugar crystal. It might be useful to review the known color types, as shown in Table 1. Even with this breakdown, it should be noted that within each of the categories or types of colorant are represented numerous sub-species as well.

In addition to the colorant types listed in Table 1, other factors, such as the amount of ash and individual ash components will have an influence. For example, ferrous iron (Fe^{+2}) can form complexes with phenolic and caramel colorant to produce even darker colorants, whereas calcium interacts with colorants to reduce the observed color by a slight amount.

Table 1. Types of sugar colorants

Color Type	General Characteristics
Phenolic	Low molecular weight colorless to light yellow precursors; darken at high pH; auto-oxidize to form yellow and brown polymers; react with polyphenol oxidase to form light yellow to dark brown colorants. Present in both beet and cane, but different molecular species in each. React with iron to make darker color. Both cane and beet are high in phenolics, but beet phenolics tend to contain nitrogen and cane phenolics do not.
Caramel	The result of thermal degradation of sucrose; low net charge; wide color range from yellow to brown; molecular weight 500 to about 1000; molecular weight and color increase as thermal destruction proceeds.
ADF	Alkaline degradation products of fructose; similar to caramels, but much darker in color.
Melanoidin	Reaction products of amino acids with reducing sugars; also known as browning reaction products; reaction occurs rapidly at alkaline pH and products are very dark brown.
Melanin	Reaction products of amino acids with phenolics; very dark. Also, black enzymatic oxidation products of phenolics (found in cane leaf juice). More common in beet sugar colorant.
Colorant-Polysaccharide complex	In cane juice (we do not know about beet colorant in this respect), the indigenous polysaccharide has phenolic groups and dicarboxylic functionalized lipids that can bind with colorant to make a very high molecular weight complex. Occludes preferentially in crystal.

The Significance of High Molecular Weight Colorant

Over the years, many research studies have indicated that for both beet and cane sugars, the relatively high molecular weight colorants are preferentially included within the sugar crystal, while the lower molecular weight species are on the surface (Tu *et al.*, 1977; Roberts and Godshall, 1978; Smith, 1966; Smith *et al.*, 1981). Clarke and Blanco (1986) showed that cane sugar colorant with a molecular weight greater than 20,000 daltons was relatively higher inside the crystal than in the syrup coating on the outside of the crystal, as determined by laboratory washing of raw sugar crystals.

Beet sugar colorant in white sugars was reviewed by Shore, *et al.*, in 1984, and further reported by Broughton, *et al.* (1986). They concluded that relatively high molecular weight colorants (1000 to 5000 daltons) are incorporated into the white sugar crystal while medium to low molecular weight colorants are found both inside and on the surface of the crystals. They also concluded that thick juice color originates mainly from that present in the juice (therefore, from the beet plant) (62%) and that formed during evaporation (18%), together accounting for 90% of the total color. A later study

on white beet sugar color by Godshall, *et al.*, (1991) showed that lower quality white beet sugars (those with higher color) also had a higher proportion of very high molecular weight colorant (above 20,000 daltons). It was shown in this study that the amount of polysaccharide in the very high molecular weight fraction of white beet sugars was very low compared to cane sugars, in which the polysaccharide in raw sugar represents at least 30-50% of the total nondialyzable fraction and increases to 80-95% of the total in white sugars (Godshall, *et al.*, 1989).

In a study of the colorants and polysaccharides in raw cane sugars (Godshall, *et al.*, 1987), it was shown that after affination of raw sugar, 66% of the remaining colorant had a molecular weight greater than 20,000 daltons and that an average of some 70% of the total polysaccharide in raw sugar remained after affination. Gel permeation chromatography showed that a large proportion of the cane colorant fell in the 300,000 to 500,000 dalton range and was associated with polysaccharide.

In another study, the proportion of high molecular weight colorant was shown to increase across the refinery (Godshall and Clarke, 1988), as shown:

Proportion of color >20,000

Raw sugar	30 - 40%
Washed raw sugar	43 - 83% (this represents colorant inside the crystal)
Refined sugar	60 - 100%

Several observations come to mind when reviewing this work on sugar colorant. First is the importance of high molecular weight colorant in transfer of color to the crystal; second is the prevalence of polysaccharide in cane sugars compared to its much lesser concentration in beet sugar; third is the disparity in what constitutes high molecular weight colorant in cane versus beet sugars. The high molecular weight colorant in beet is reported as ranging from 1000 to 5000 daltons (Broughton, *et al.*, 1986) or 12,000 to 30,000 (Godshall, *et al.*, 1991); whereas for cane colorant, the majority of colorant is over 300,000 daltons.

Transfer of Color

A colorant (or any impurity) can be transferred to the crystal by three mechanisms: (Grimsey and Herrington, 1996):

1. It can absorb onto the crystal surface;
2. It can co-crystallize into the crystal matrix;
3. It can be trapped by liquid inclusions inside the crystal.

The scope of this presentation is concerned mainly with the second mechanism, the co-crystallization, or occlusion/transfer, of colorant inside the crystal.

Various terms have been used to describe the transfer of colorant into crystal from syrup during the crystallization step, or conversely, its elimination from the crystal: The elimination factor of Carruthers (1961); color transfer factor of Chiu and Sloane (1980); the impurity transfer of Lionnet (1987); the inclusion rate of Dmitrenko and Brenman (1992); the transfer factor of Donovan and Williams (1992).

Grimsey and Herrington (1996) also determined a transfer factor and used model colorants in their studies. They used the color transfer to ash transfer ratio as a measure of incorporation of colorant into the crystal, assuming that ash transferred the least. KCl was used as the ash component in their model.

Table 2 shows the transfer ratio of the colorants Grimsey and Herrington examined. A higher transfer ratio indicates greater incorporation into the crystal. They also imply that for a compound to be included in the crystal, it must be able to form a complex with sucrose in solution.

Table 2. Transfer ratio of some model colorants into sucrose crystal. A higher transfer ratio indicates greater incorporation of colorant into the crystal. (From Grimsey & Herrington, 1996)

Transfer ratio (colorant/ash)	Model Colorant
1.4 - 1.5	Glucose-glycine (a synthesized melanoidin)
7.2	Sugar caramel
11.5	Caramel 15461 with weak negative charges (commercial product)
14.0	Caramel 15639 with a positive charge (commercial product)

Dmitrenko and Brenman (1992) determined that colloids and other high molecular weight compounds, having more hydration than single ions, were included to a greater extent in the sugar crystal.

A lot of work has been done in South Africa by Lionnet on the transfer of sugar colorant into raw sugar (Lionnet, 1987; 1988; 1991). His studies have shown that more colorant transfers into raw sugar during the beginning and the end of the crop season, reflecting the quality of the juice, and very likely the increased load of polysaccharides, leaves and trash that occur at these times.

Additionally, the famous work of Mantovani and colleagues in Italy on the inclusion of coloring matter in crystals and its effect on crystal morphology, should be mentioned (Mantovani, *et al.*, 1977; 1986).

Based on many years of work done at Sugar Processing Research Institute, Inc., with Louisiana mills, it has been possible to determine the transfer coefficient of various minor components from the raw cane juice into the raw cane sugar, as shown in Table 3. This represents standard milling operations with standard clarification techniques and is true for the A sugar.

Table 3. Percentage of component in raw cane juice that will remain in the raw sugar.

Juice Component	Percent that remains in Raw Sugar
Starch	30 - 50%
Dextran	30 - 50%
Indigenous Cane Polysaccharide	20 - 30%
Color	10 - 20%
Ash	5 - 10%

It becomes evident, looking at this list, that carbohydrate-type material has a greater tendency to be occluded in the crystal. Also, the higher the molecular weight, the greater the tendency to be occluded in the crystal. This small demonstration shows that the lower the incoming material in cane juice, the lower the amount of these impurities in the raw sugar. But it also shows that different mechanisms are at work to determine how much of any particular component will transfer into the raw sugar crystal.

In another study (Godshall, *et al.*, 1988), the removal of specific colorant and polysaccharide species, using gel permeation chromatography (GPC) was used. These data are summarized in Table 4. It is evident that polysaccharides are more difficult to remove and that colorant most associated with polysaccharide is also more difficult to remove. Phenolic related colorant is easier to remove than nitrogen-related colorant.

Research by S.P.R.I. and others have shown that high molecular weight species are implicated in color formation. At SPRI, it was shown that the indigenous sugarcane polysaccharide (ISP) has the tendency to complex with color and "pull" color into the crystal with itself.

The other element of interest is that, while color as a whole transfers 10-20% into the crystal, color is not one entity as already discussed, and some types of color have a greater or lesser affinity for the crystal. The goal of research is to identify those color types with the highest occlusion/transfer index and either to work out purification methods that remove them preferentially, or else to prevent or inhibit their formation in the first place. Which of these latter two options is used will depend on the nature of the colorants that need to be controlled.

If, as research by SPRI and others indicates, part of the problem is the presence of polysaccharides, then these polysaccharides, which are indigenous to the cane and beet plant and are therefore naturally going to be present in the juice, will have to be controlled by methods that exclude or remove them preferentially, such as membrane filtration methods or enzymatic treatment.

Table 4. Proportion of impurities remaining in white sugar relative to the raw sugar.

Colorant species	% Remaining in white sugar
ICUMSA color	0.3
Very HMW color >1,000,000 Da	1.1
300,000 - 800,000 Da color	0.6
~ 30,000 Da color	2.1
Total polysaccharides	33.6
Very HMW polysaccharide >1,000,000 Da	24.6
~30,000 Da polysaccharide	11.9
Phenolics	10.6
Amino nitrogen	24.1

Little research has been reported in the literature on the effect of turbidity in color formation. An early study reported that removal of turbidity from clarified cane juice resulted in a 40% reduction in color in the resultant sugar (Fort and Smith, 1954). In work at SPRI, Robert, *et al.* (1994), showed that the lipid fraction of cane juice turbidity (representing about 20% of the total mass of the turbidity) caused a great increase in the color of a boiled white sugar and formed a lot of color on heating.

Beet Standard Liquor Colorant Compared to Molasses Extract Colorant

As mentioned above, color *per se* is not the only criterion for occlusion of color in crystals, as shown by the observation that beet standard liquor of 2000-3000 ICU color can produce a 20-30 ICU color white sugar on boiling; a beet molasses chromatography extract of color 6000-7000 ICU will also produce low color white sugar; but a cane sugar final syrup can only have a color of about 200-300 to produce this low color of white sugar.

A comparison of the colorant factors in several samples of beet standard liquor and beet molasses chromatography extract was conducted at SPRI, with the results shown in Table 5. While the color is almost three times higher in the chromatography extract, the turbidity, the concentration of high molecular weight species (the nondialyzable portion), the total polysaccharides and the carbohydrate proportion of the high molecular weight complex are all much higher in the standard liquor. The difference is particularly noticeable for the polysaccharide concentration, which is almost 4 times higher in the standard liquor compared to extract (1112 ppm vs 290 ppm, on average).

Table 5a. Factors that influence color transfer in crystals -- comparison of beet standard liquor vs. beet molasses chromatographic extract.**Standard Liquor**

Parameter	10/26/98	12/14/98	2/19/99	Mean
Color	1815	1951	2864	2210
Turbidity	381	302	411	365
Nondialyzable* (ppm)	1981	1127	4052	2387
Total Polysaccharides, ppm	776	838	1723	1112
% CHO in ND**	55.7	55.8	73.4	61.6

* Nondialyzable = all soluble material >12,000 DA molecular weight

** % CHO in ND = % carbohydrate content of nondialyzable material

Table 5b. Factors that influence color transfer/occlusion in crystals -- comparison of beet standard liquor vs. beet molasses chromatographic extract.**Chromatography Extract**

Parameter	10/26/98	12/14/98	2/19/99	Mean
Color	6006	5547	6815	6123
Turbidity	193	107	157	152
Nondialyzable* (ppm)	1200	726	578	835
Total Polysaccharides, ppm	244	223	404	290
% CHO in ND**	41.4	32	37.5	37

* Nondialyzable = all soluble material >12,000 DA molecular weight

** % CHO in ND = % carbohydrate content of nondialyzable material

For ease of comparison, the data shown for the three across-season samplings of beet standard liquor and chromatography extract are shown averaged in Table 6; also shown is the ratio of the standard liquor to extract for each of the parameters.

Table 6. Mean values of parameters in three across-season samples of beet standard liquor compared with molasses desugarization extract.

Syrup Type	Color	Turbidity	HMW >12,000	Total Polys	%CHO/HMW
Standard Liquor	2210	365	2387	1112	61.6
Molasses Extract	6123	152	835	290	37.0
Standard/Extract	0.36	2.4	2.9	3.8	1.7

The visual appearance of the non-dialyzable material (all material above 12,000 daltons, called the “tenate”) was strikingly different for the two types of liquor. The thick juice standard liquor tenate was voluminous and fluffy, and pale beige in color. The molasses desugarization extract was much less in volume, more compact in nature and very dark brown. The data in Table 5, showing the carbohydrate composition of the tenate explains the difference in appearance. The high carbohydrate content of the standard liquor tenate is indicated by the fluffy and voluminous nature of the tenate; the molasses extract tenate has much less carbohydrate, being mostly pure colorant in nature, hence its more compact nature and dark color.

The difference between the two types of samples reflects the separation techniques used. In chromatography, there is a much finer and more perfect separation of constituents due to the very nature of chromatography. Thus, the high molecular weight components, which are excluded, are easily separated from the bulk of the sugar. Standard liquor, not having the benefit of specific separation techniques, carries over more of the high molecular weight components present in the clarified beet juice.

Researchers at Audubon Sugar Institute in Louisiana (Saska, *et al.*, 1995) observed in studies on membrane filtration of clarified cane juice, that once the turbidity and much of the polysaccharide was removed, the cane syrups behaved more like beet syrups in that they could boil a white sugar from a much higher color syrup than the conventional.

The Fluorescent Nature of Sugar Colorant

It has long been known that sugar colorant fluoresces, and that this property could be used to provide information about the nature of the different types of sugar colorant (Carpenter and Wall, 1972).

The group at the Royal Veterinary and Agricultural University of Denmark, under the tutelage of Prof. Lars Nørgaard, has extensively studied the fluorescent nature of sugar beet colorants, and more recently the nature of cane sugar colorants and model colorants. Fluorescence of sugar colorants is the topic of another presentation in this conference.

Standard liquor and molasses extract samples from 10/26/98 and 12/14/98, discussed above, were analyzed by measuring the fluorescent landscapes of solutions diluted to 1 and 2 Brix, at pH 7. The excitation range was 230-420 nm with 10 nm intervals and the emission range was 278-530 nm.

Figure 1 shows the contour plots of the molasses chromatography extract. Figure 2 shows the contour plots of the standard liquor. The red color indicates the most intense color while the yellow represents less intense color. The blue areas indicate no colorant activity. Because of the intensity of the colorant even at these concentrations, it was necessary to do a dilution series, as quenching of components can occur at too high concentrations. The dilution series consisted of six samples, beginning with a 2 Brix solution and then 5 dilutions in succession made from a 1:2 (w/w) ratio with water, with all solutions adjusted to pH 7. The PARAFAC program used to resolve the data showed that a 4-component model was the best result.

The concentration profiles showed that the dilution of the samples reduced the concentration quenching in the ultraviolet area, allowing a new component to appear ($\lambda_{\text{ex}} / \lambda_{\text{em}} = 274/305 \text{ nm}$), which was not visible in the first two extract solutions (Figure 1). The four profiles found were very similar for both the extract and the standard liquor both in excitation-emission maxima and in the spectral outline. The excitation-emission maxima for the four components are shown in Table 7, with some speculation of a very preliminary nature about the nature of the colorants represented.

Table 7. The fluorescent components in beet colorant from molasses chromatography extract and standard liquor.

Excitation max., nm	Emission max., nm	Possible composition
275	305	Tryptophane/tyrosine reaction products
285	360	Tryptophane/tyrosine reaction products
330	420	Small polymer system
380	460	Larger polymer system

A combined 4-component model was made from all the samples, and is shown in Figure 3. The result is a combination of the extract profiles and the standard liquor profiles. It is noted that the concentration level of the extracts was about a factor of 2 higher than the level of the standard liquors.

The conclusion from these findings is that it was not possible to find any differences between the fluorophores from standard liquor and from molasses extract. This finding was thought to be contradictory at first, but given the great differences in polysaccharides and turbidity in the two types of samples, we are compelled to rethink the idea that the nature of the beet colorant is fundamentally different in standard liquor vs. chromatography extract. We are now focusing on the polysaccharide portion as being responsible for a significant transfer of color into crystals.

Crystallization Study

The first part of this report has dealt with characterizing the chemical composition of colorants in order to understand their behavior. Other ways to elucidate the nature of colorant include observation of its behavior under controlled laboratory tests that simulate processing conditions.

The decolorization of sugar-containing solutions generally can be classified into four processes, each of which tells us something about the nature of colorant, its reactivity, its position in or on the crystal, etc. These general processes are listed here:

- 1) Mechanical separation (e.g., affination)
- 2) Primary decolorization by chemical means (carbonation, phosphatation, ozone, hydrogen peroxide.)
- 3) Secondary decolorization by adsorption (granular activated carbon, ion exchange resin, bone char)
- 4) Crystallization

In this experiment we studied the nature of colorant by measuring the transfer of color into the sugar crystal during the crystallization process. We have defined color transfer as the percentage of color found in the sugar crystal relative to the color of the feed. SPRI has carried out some crystallization studies under laboratory conditions. The results are shown in Table 8.

Table 8. Sugar boiling at SPRI using a bench scale vacuum pan.

Material	Feed Color	Crystal Sugar Color (2% washing)	Color Transfer
Clarified cane syrup (mill)	11,376	691	6.1%
Clarified cane syrup (mill)	9217	582	6.3%
Beet standard liquor	2864	29	1.0%
Beet molasses extract (MD plant)	6815	77	1.1%

The results indicate that the transfer of cane colorant is significantly higher than that of beet colorant, 6% vs 1%. One goal of research would be to determine factors that decrease the transfer index of cane colorant.

Effect of Heating on Color Formation

Another way to characterize the nature of colorant is to study the effect of heating to determine the thermal stability of the colorant.

Table 9 shows the results of experiments that tested the effect of heating on color formation. The syrups, at 50 Brix, and pH 8.5-8.7, were heated at 95° C for one hour. The total polysaccharide (TPS) concentration is also shown for these sample. The cane samples and the beet standard liquor, all high in polysaccharides, increased in color by 5-6%, whereas the beet molasses extract did not change significantly. The data indicate that a high level of TPS may contribute to color formation. However, the correlation is not based solely on TPS concentration, since the TPS of the affination syrup, at 6999 ppm, was 4.5 times higher than that of the raw sugar, yet the increase in color was the same. Also, the TPS of the beet standard liquor was slightly higher than that of the cane raw sugar, yet the color increase was slightly less. These differences may have a correlation with the turbidity, considering the discussion on turbidity given above. The color increase of 4.7% in the beet standard liquor may not be significantly different from the 6.3% increase of the two cane samples, in spite of wide disparities in starting color. The extract color did not change on heating, showing thermal stability.

Table 9. Effect of heating on color formation (95° C, 1 hr)

Sample	Brix	TPS*	Original color	Color after heating	% Increase in color
Affination syrup (cane)	50.16	6999	40,365	42,900	6.3
Raw sugar (cane)	50.86	1558	7577	8053	6.3
Beet Std. Liquor	50.40	1723	3070	3214	4.7
Beet Molasses Extract	51.61	404	7291	7309	0.25

*TPS = Total polysaccharide, ppm based on Brix solids

Summary

This paper has summarized some factors that elucidate the nature of beet and cane sugar colorant, showing some of the differences between the two. The goal of future research would be to determine ways to decrease the transfer index of cane sugar colorant so that white sugars may be boiled from higher color feed liquors.

The importance of high molecular weight colorant and polysaccharides in color transfer was discussed. The thermal stability of highly colored molasses extract colorant was shown relative to that of thick juice standard liquor and cane syrups. Fluorescence studies showed that there is no significant difference in the profiles of beet standard liquor and chromatographic extract.

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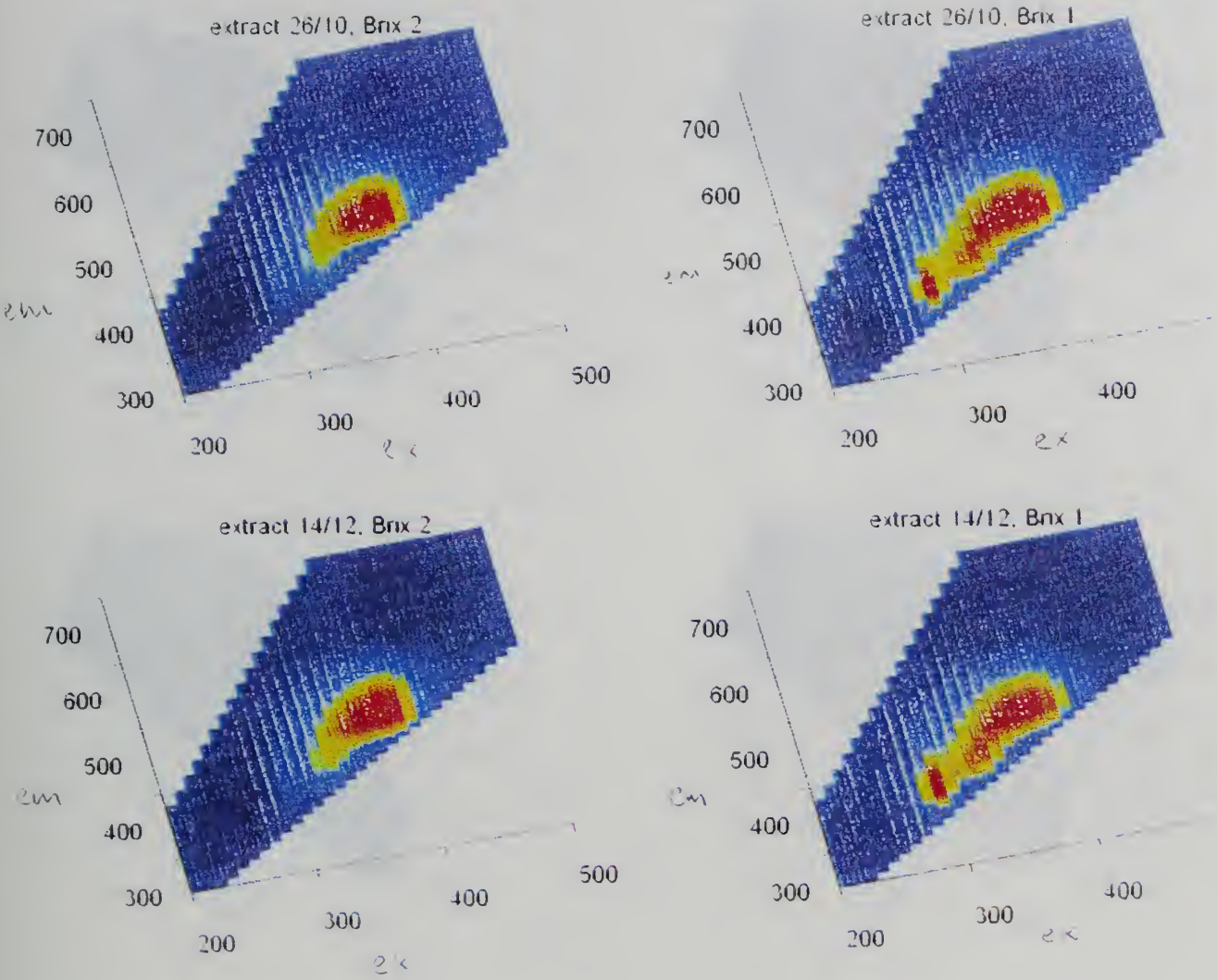


Figure 1. Fluorescent profiles of colorant in molasses chromatographic extract.

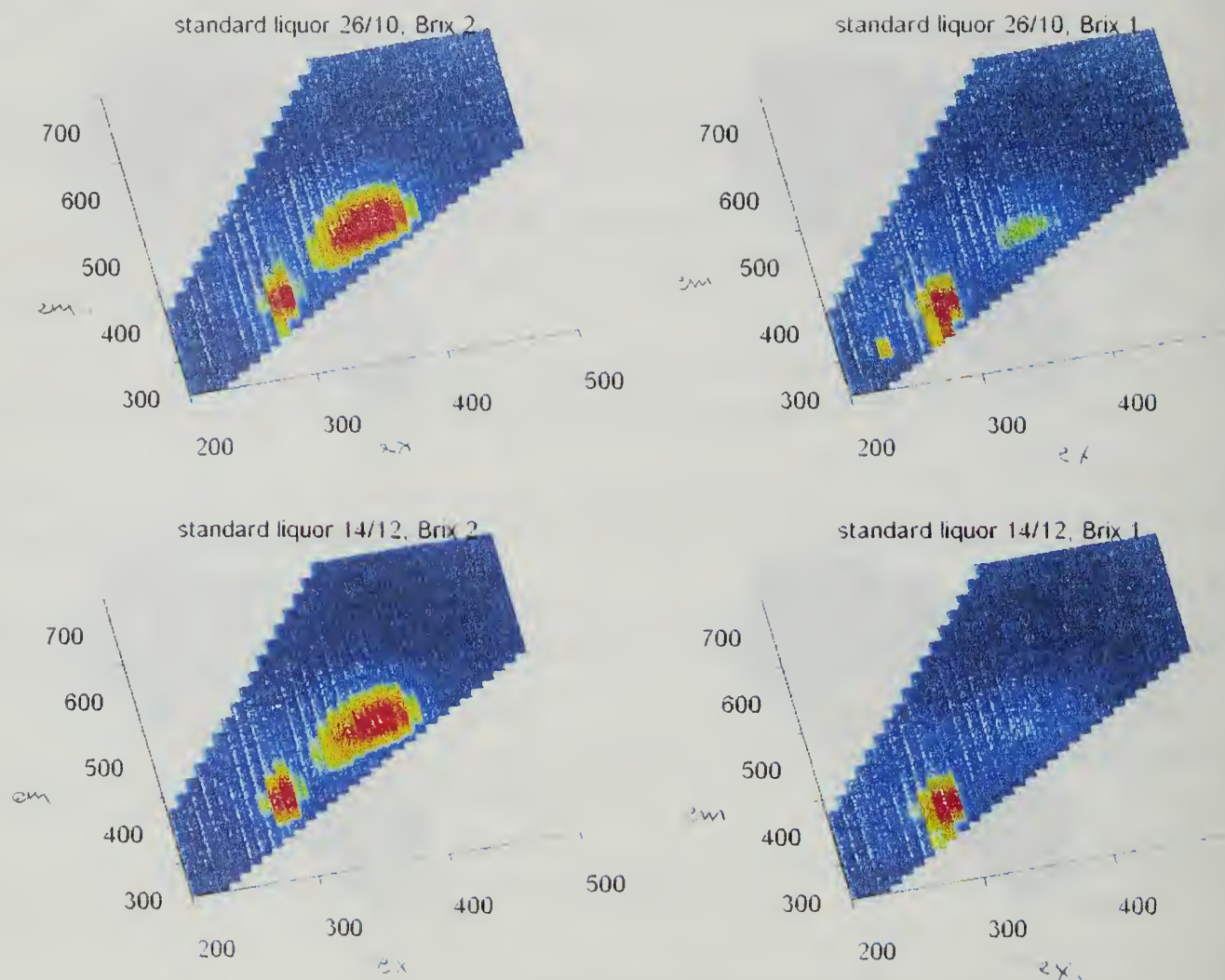


Figure 2. Fluorescent profiles of colorants in beet thick juice standard liquor.

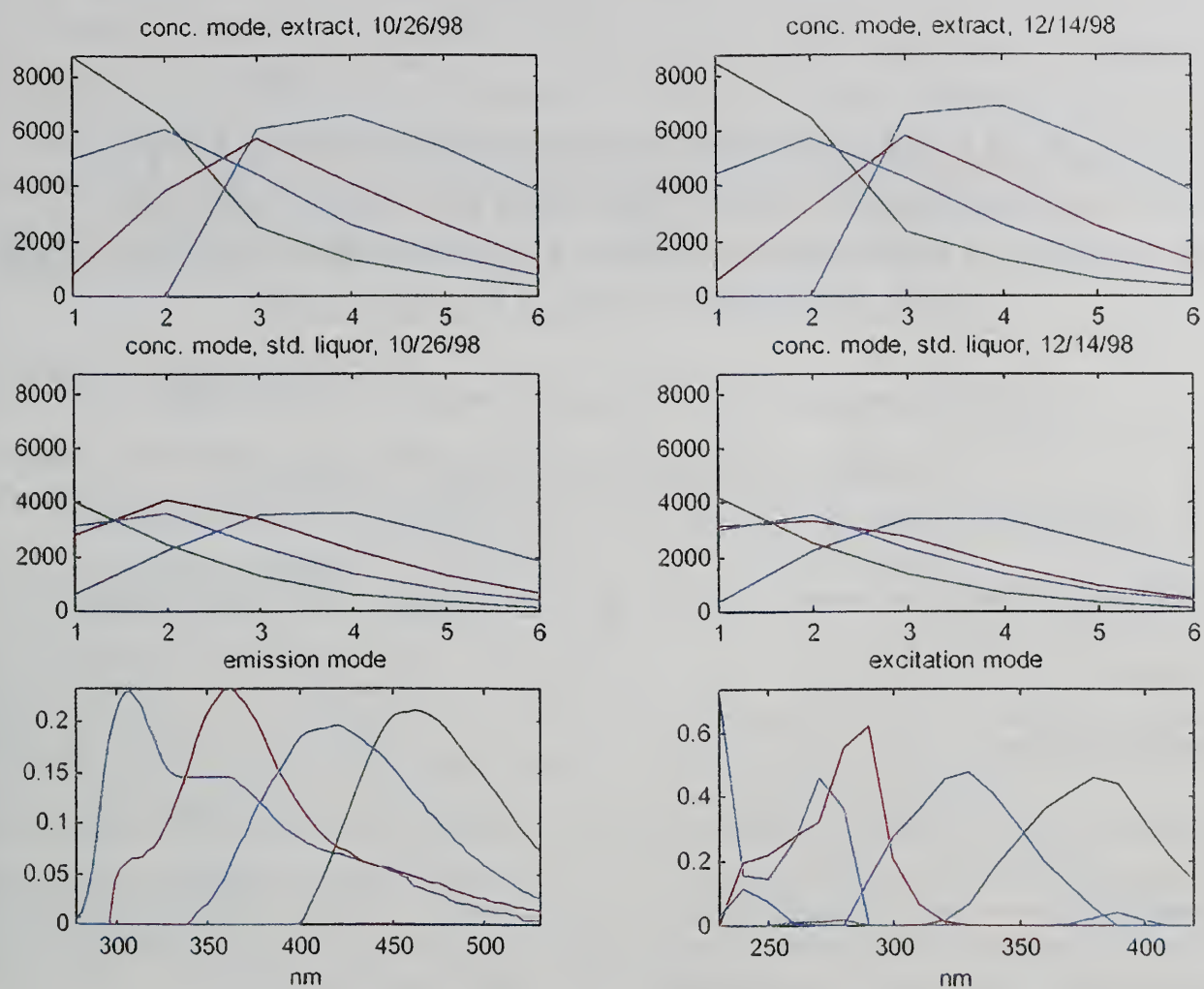


Figure 3. Combined 4-component model of beet sugar colorant.

ANALYSIS OF FLUORESCENT COLORANTS AND COLOR PRECURSORS IN CANE SUGAR MANUFACTURE USING SPECTROFLUOROMETRY AND MULTIVARIATE DATA ANALYSIS

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INTRODUCTION

It has been known for years that commercial sugar exhibits fluorescence. In 1972 Carpenter and Wall measured fluorescence emission spectra at several excitation wavelengths of sugar process samples. Excitation-emission contour plots were inspected and they found a characteristic emission peak pattern in the samples. However, they could only base their conclusions about the chemistry in the samples on visual comparisons of dominant fluorescence peaks.

With the use of multivariate statistical methods (chemometrics), it has become possible to extract relevant chemical information hidden in the spectral data. Fluorescence spectroscopy has proved to be an effective screening method in the beet sugar manufacturing process when applying appropriate chemometric models to the multivariate data (Munck *et al.*, 1998). In a study of fluorescence spectra of beet sugar samples, classification (soft independent modelling of class analogy, SIMCA) models of the samples according to factory and calibration (partial least squares regression, PLS) models of quality parameters provided information about the chemistry in the samples with regard to the composition of the sugar beet raw material, as well as the influence of the process (Nørgaard, 1995).

Another study of beet sugar fluorescence utilized the three-dimensional structure of fluorescence excitation-emission landscapes to resolve spectral excitation and emission profiles of fluorophores in sugar with a multi-way chemometric model, PARAFAC (Bro, 1999). Four fluorescent components were found that captured the variation in the fluorescence data of sugar samples collected from a factory during a three-months sugar campaign. The concentrations of the four components estimated from the sugar samples could be correlated to several quality and process parameters, e.g. color, ash and pH, and they were characterized as potential indicator substances of the chemistry in the sugar process.

In the light of the promising results from the fluorescence studies of beet processing, similar studies of fluorescence in cane sugar processing were initiated. One of the projects aims was specific excitation/emission wavelength recognition by analyzing the fluorescence landscapes of a sample set of raw sugars with the use of chemometrics. Another study comprised basic color identification using model colorants to identify the fluorescent profiles of components associated with specific kinds of colorants, such as caramels and Maillard products. In addition, the change in fluorescence through sugar processing was examined by comparing fluorescent components in a set of sugar processing samples from a cane sugar factory. Two-way (PCA, PLS) and three-way (PARAFAC) chemometric methods were used in the data analyses.

MATERIALS AND METHODS

For details of the raw sugar study and the model colorant study, the reader is referred to Baunsgaard *et al.* (2000a) and Baunsgaard *et al.* (2000b), respectively.

Cane factory process samples

A set of process samples was collected throughout a cane sugar factory one day in the 1998 sugar campaign in Louisiana, USA. The sample set from the cane factory consisted of nine samples: diluted juice, clarified juice, evaporator syrup, A-sugar, A-molasses, B-magma, B-molasses, C-magma and C-molasses. In Table 1 the dilution levels of the samples used in the fluorescence measurements are shown together with ICUMSA color, Brix and pH of the samples. All samples were frozen shortly after they were taken in the production.

Fluorescence landscape measurements

The fluorescence measurements were performed on a Perkin-Elmer LS50 B fluorescence spectrometer. Landscapes were recorded by scanning emission spectra at successive excitation wavelengths at predefined intervals. Some of the measured areas in the landscape do not conform to true fluorescence response, such as the Rayleigh scattering peaks, and they were removed and treated as missing values. In Fig. 1 a fluorescence landscape of a raw sugar sample is displayed at 21 excitation wavelengths in the range 250-450 nm with a 10 nm interval and the emission range was 298-520 nm at 3 nm steps. All samples were diluted to a concentration level below the concentration quenching of the fluorescence. All samples were measured at pH 7.

Data analysis

A two-way structure of the fluorescence landscapes (samples x wavelengths) was obtained by unfolding the landscape of each sample so that the emission spectra were arranged in the order of the excitation wavelengths and the missing areas were removed. An unfolded landscape is shown in Fig. 2. Principal component analysis (PCA) is used to find the principal directions of variation in the fluorescence data (Martens and Næs, 1993). For each principal component, a loading common for all the samples is extracted from the unfolded fluorescence data where the scores reflect the contribution of that loading in each sugar sample. Another two-way method, partial least squares regression (PLS), is used to make predictions of the quality parameter color from the unfolded fluorescence data (Martens and Næs, 1993).

Table 1. Chemical parameters of the cane factory sample set

Samples	pH	Brix	Dilution (w/w) ^a	ICUMSA color
Dilute juice	5.1	10.5	1:16	14836
Clarified juice	7.2	12.0	1:64	11941
Evaporator syrup	7.1	67.6	1:640	12610
A-sugar	7.1	100.0	1:80	1637
A-molasses	6.6	70.2	1:1600	24732
B-magma	6.4	92.2	1:640	8787
B-molasses	6.2	87.8	1:1600	35174
C-magma	5.7	91.8	1:1600	31542
C-molasses	5.6	86.2	1:3200	35900

^a The dilution level where there was no apparent concentration quenching of the fluorescence.

The three-way structure of the fluorescence landscape data from several samples (samples x excitation wavelengths x emission wavelengths) has the advantage that decomposition models may be used, which give an easier interpretation of the resulting loadings. Whereas the orthogonal loadings from PCA and PLS models of the unfolded fluorescence data are difficult to interpret, the multi-way decomposition model PARAFAC (parallel factor analysis) decomposes three-way fluorescence data into spectral excitation and emission profiles in terms of pure components (Bro, 1997). The two-way data analyses were performed using Unscrambler 7.01 (CAMO ASA) and the implementation of the PARAFAC model was obtained from The N-way Toolbox for MATLAB (Andersson and Bro, 1999).

RESULTS AND DISCUSSION

Fluorophores in raw cane sugar

The study of raw sugar fluorescence involved a sample set of raw sugars from all over the world, which ensured that the chemometric models were not susceptible to local variation of raw material or production methods (Baunsgaard *et al.*, 2000a). The sugar samples were also spread over forty production years and this was used to study the formation of color during storage. A four-component PARAFAC model turned out to be the best model based on the three-way fluorescence landscape data of the raw sugar samples (Fig. 3). However, two of the components (330/400 nm and 360/420 nm) had very similar emission spectra, and it was suggested that these two components represent the same type of colorant fluorophore but was separated into two fluorophores due to wavelength shifts in the spectra. Two-way models (PCA, PLS) based on unfolded fluorescence landscapes of the raw sugar samples supported that three significant fluorophores are responsible for the fluorescence in raw sugar with approximate excitation and emission maxima of (275/350) nm, (340/420) nm and (390/460) nm. The raw sugar fluorescence

does not appear to contain the same information about factory or geographical origin as beet sugar fluorescence did, but an age distribution of the samples in a PCA score plot (Fig. 4) showed that the color formed during storage is related to the fluorophores, especially the color precursor at (275/350 nm). The two other fluorophores have colorant characteristics and all three fluorophores are correlated to ICUMSA color.

Model colorants fluorophores

Fluorescence measurements of model colorants were undertaken to obtain fluorescent profiles of reaction products of known color reactions to be compared with similar profiles obtained from process samples (Baunsgaard *et al.*, 2000b). Accordingly, fluorescence landscapes of model colorants were measured and individual components were resolved with PARAFAC. Browning mixtures from the Maillard reactions of glucose-glycine and glucose-lysine as well as degradation products from fructose and glucose were the chosen model systems. The resolved emission spectra of the fluorophores from the various model colorant samples were practically all located in the visible wavelength area and their spectral appearances were quite similar (Fig. 5). It was concluded that the small differences in the fluorophores were more dependent on the reactivity and ratio of the reactants, and thus on the formation of darker color, than on differences in reaction products.

Fluorescence changes in sugar cane factory samples

In the light of the above results, the measurement of fluorescence of process samples from a raw sugar factory may be used to monitor the development of color in the process. Consequently, PARAFAC models were made from fluorescence landscapes of the process samples and three components were the optimal number in all the models (Fig. 6). The model results show that the profiles of the components in the various process samples are quite similar. Except for diluted juice, all the process samples display the same three emission peaks at approximate 360 nm, 430 nm, and 490 nm. Dilute juice fluorescence does not contain an individual fluorophore peaking at 395/490 nm, but the excitation profile of the solid component in Fig. 6 has a shoulder at approx. 395 nm, representing a small contribution from the 395/490 nm fluorophore. This suggests that the formation of this component fluorescing at the highest wavelengths with characteristics of a colorant is already taking place in the initial steps of the process.

The fluorophores from the model colorant samples shown in Fig. 5 were compared with the resolved fluorophores of the process samples by listing their excitation and emission wavelength maxima (Table 2). The maxima as well as the plotted fluorescence profiles show that some of the fluorophores found in the process samples are similar to the model colorant fluorophores, e.g. the fluorophore at approx. 325/420 nm. This fluorophore was also resolved in the raw sugar model and has previously been found in beet sugar (Bro, 1999). The 270/355 nm fluorescent component found in all the process samples has been suggested to be the amino acid tryptophan (Baunsgaard *et al.*, 2000b), which is supported by the fact that this component is not present in the model colorant samples.

The model colorants in general contain fluorescence of higher wavelengths than the process samples, and this demonstrates how difficult it is to obtain the right conditions of model systems to simulate real processes. However, there are some small changes in the process samples fluorophores through the process that resembles a color development, and the profiles of the C-

magma and C-molasses fluorophores, slightly different from the other process sample fluorophores, resemble the pattern of the model colorant fluorophore profiles, indicating a similar color composition.

Table 2. The excitation (Ex) and emission (Em) maxima of the resolved fluorescence components from the PARAFAC models of the model colorants and the cane factory process samples.

Sample	λ_{\max} (nm), Ex/Em ^a					
Dilute juice	-	270/345	275/360	320/435	-	-
Clarified juice	-	-	270/355	310/430	-	395/490
Evaporator syrup	-	-	270/355	310/430	-	395/490
A-sugar	-	-	270/360	330/430	-	395/490
A-molasses	-	-	270/355	320/430	-	400/495
B-magma	-	-	270/355	340/425	-	400/480
B-molasses	-	-	270/355	340/425	-	400/480
C-magma	-	-	265/360	(330/420) ^b	360/430	400/485
C-molasses	-	-	265/360	(330/420) ^b	360/425	400/485
Glucose degradation	280/320	-	-	320/410	370/440	400/510
Fructose degradation	-	-	-	330/430	390/450	430/530
Glucose-glycine	-	-	-	340/430	390/450	410/505
Glucose-lysine	-	-	-	340/435	390/450	410/505

^a The wavelength maxima are from the fluorophores in Fig. 5 and 6 shown from left to right.

^b Shoulder in the dotted profile in Fig. 6.

CONCLUSIONS

Fluorescence of raw sugar is correlated to ICUMSA color, and the three main fluorophores represents a color precursor of storage color and two colorants. Model colorants from the Maillard and sugar degradation reactions contain fluorescence of rather equal appearance that seems to represent the same colorant formation pathways. Process samples from a cane sugar factory showed colorant fluorescence in the earliest process stages, and the same fluorophore pattern is repeated through the process with a slight development of colorant fluorophores.

ACKNOWLEDGMENTS

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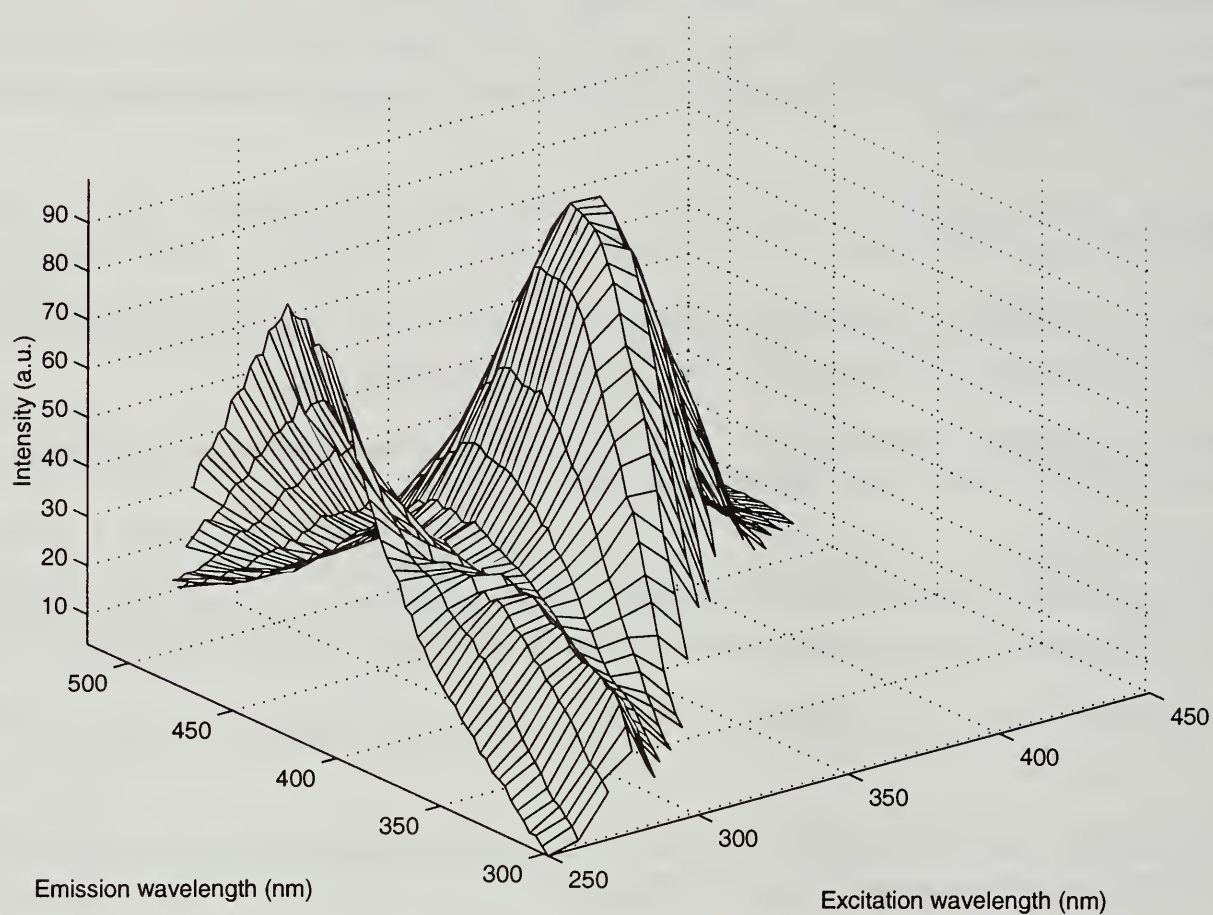


Fig. 1 Fluorescence landscape of a raw sugar sample with the excitation range 250-450 nm and the emission range 298-520 nm of a raw sugar sample. The white areas in the plot denote the missing data areas.

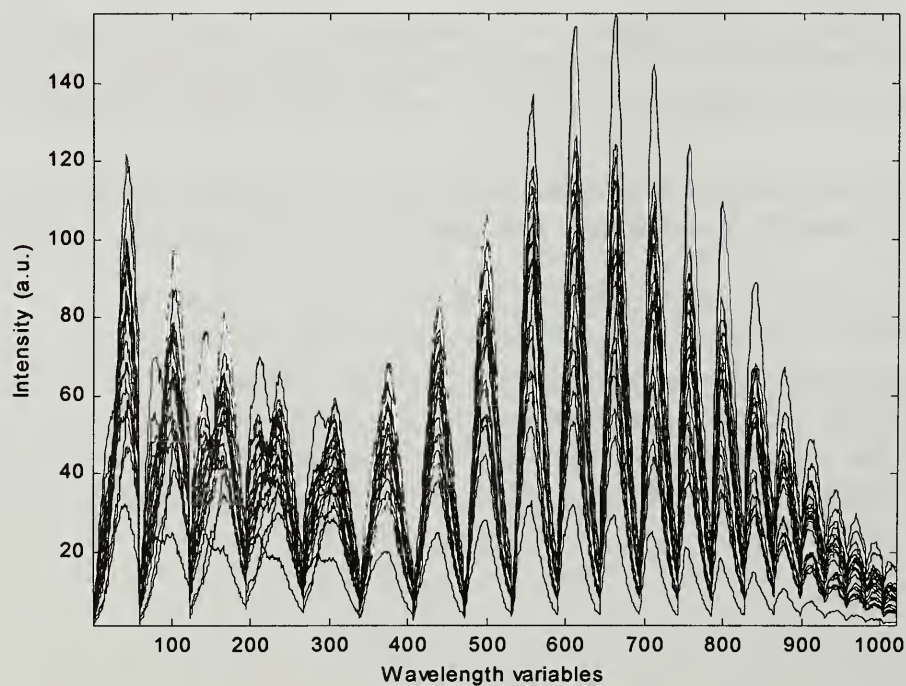


Fig. 2 An unfolded fluorescence landscape.

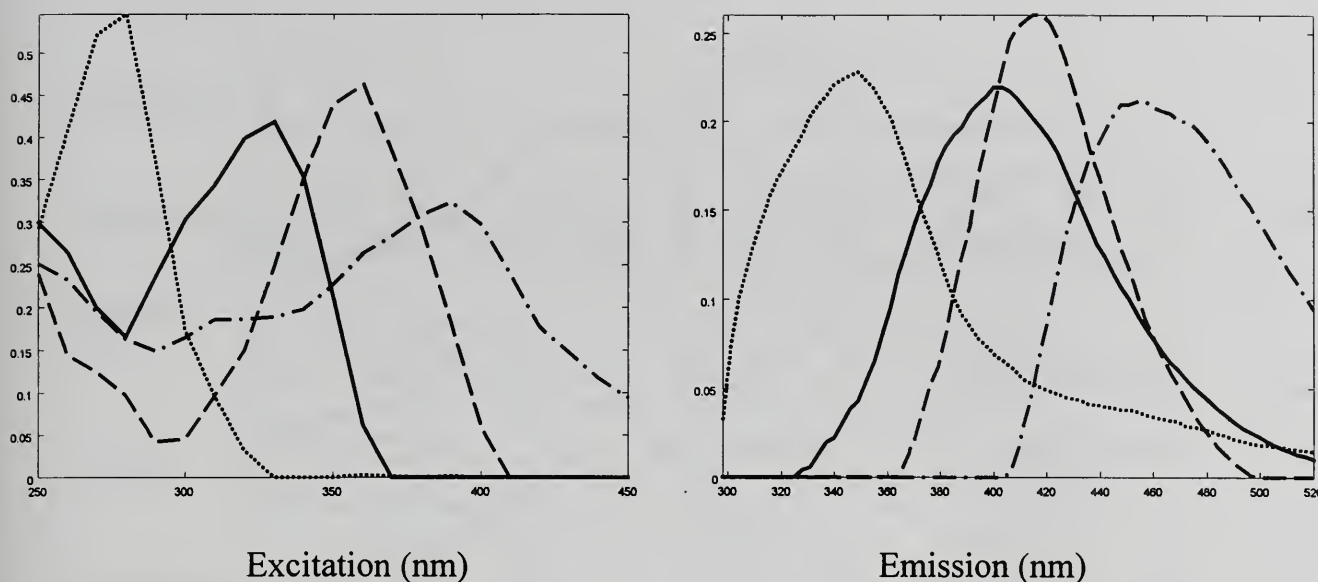


Fig. 3 Spectra resolved from a 4-component PARAFAC model of raw sugars. Excitation/emission maxima: (···) 275/350 nm, (—) 330/400 nm, (---) 360/420 nm, and (-·-) 390/460 nm. All spectra have been normalized to unit length

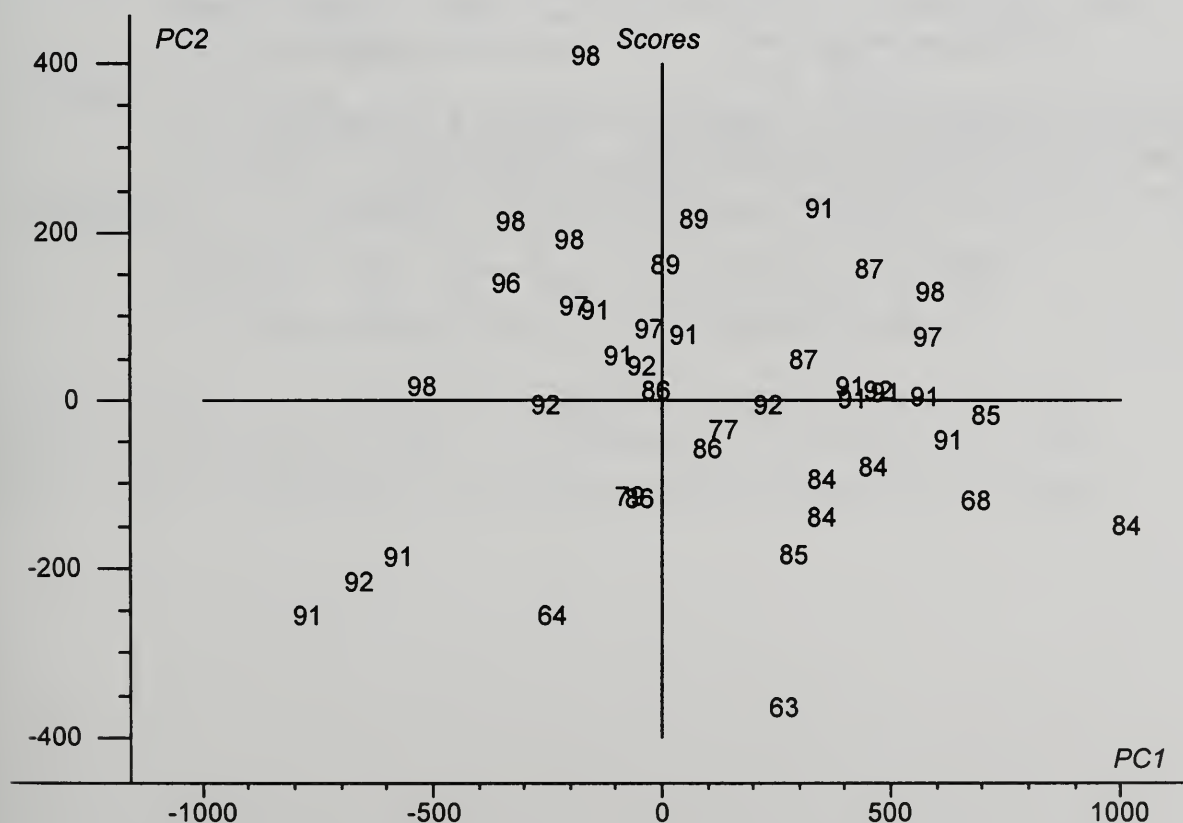


Fig.4 PCA score plot of raw sugar samples showing the distribution of raw sugar samples according to production year along principal component 1 (PC1) and principal component 2 (PC2).

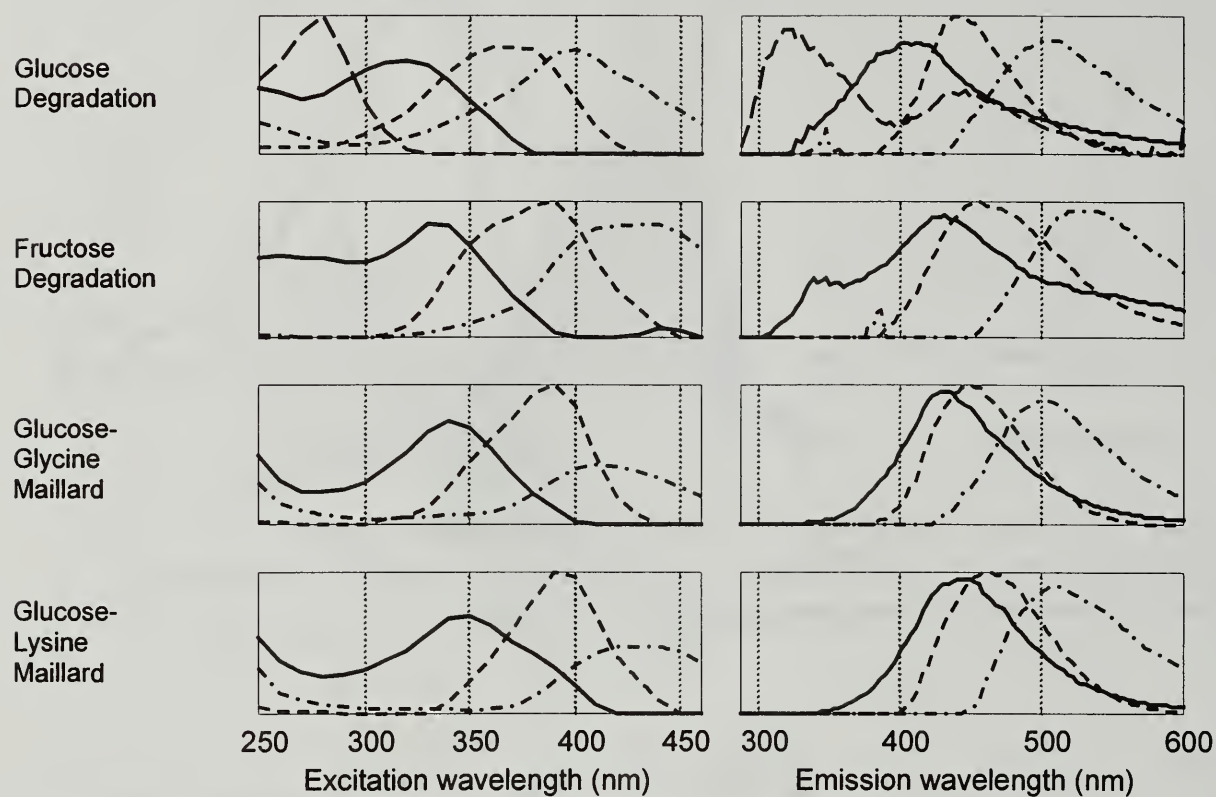


Fig. 5 Resolved spectra from the PARAFAC models of the measured fluorescence landscapes of model colorants. Excitation/emission maxima: 280/320 nm (---), 320-340/410-435 nm (—), 370-390/440-460 nm (---), and 400-430/485-530 nm (---).

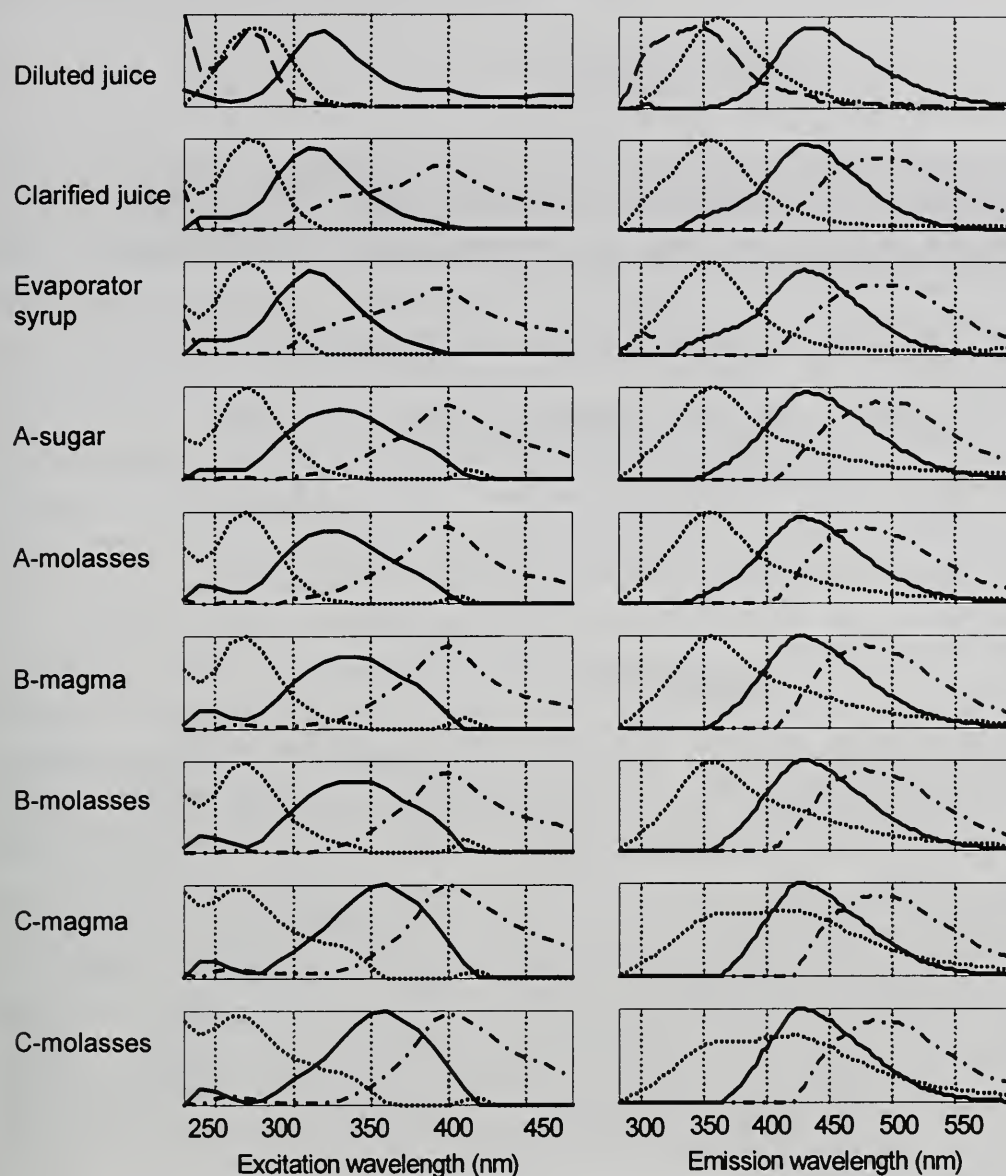


Fig. 6 Spectra resolved from PARAFAC models of cane factory process samples. Excitation/emission maxima: approx. (--) 270/345 nm, (...) 270/360 nm, (—) 320-360/430 nm, and (- - -) 395/490 nm. All spectra have been normalized to unit length

RELATIONSHIP OF REDUCING SUGARS (INVERT) TO SUCROSE RECOVERY AND STABILIZATION

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ABSTRACT

During sugar manufacturing processes, chemical changes occur that affect sugar yield and product quality, mainly sucrose loss, invert gain and invert loss correlated with color gain. Although invert is destroyed in beet raw sugar processing and in carbonatation refining, cane raw sugar factories and phosphatation refineries continue to deal with the effect of invert on processing efficiencies. Environmental concerns related to carbonate cake disposal have generated new research into alternative processes to carbonatation, both in beet and cane sugar production. If these new processes do not reduce or eliminate invert, then invert problems will become apparent with these systems. Experimental objectives were to study sucrose conversion to invert sugar and other species correlated with changes in color under acid conditions, conversion of invert to color compounds under alkaline conditions, and to determine how invert concentration affects color and sucrose loss under various process stream conditions.

Pure sucrose solutions of 65 and 15 Brix were spiked with invert (glucose and fructose or fructose alone) levels of 0-4 % at pH 6-9, and incubated 85°C for 0-6 hr. Samples were analyzed for color (ICU), final pH, and residual invert (HPIC). At 65 Brix and pH below 7.5, there was no detectable change in color, but samples showed as much as a 25 % increase in invert sugars. At pH 8.0, there was no change in color or conversion of sucrose to invert sugars. At pH 8.5 and higher, there was rapid color increase in direct correlation with a reduction of residual invert. At 15 Brix and 1.0% invert/fructose, color changes were less pronounced but correlated with invert gain and loss at varying pH similar to the 65 Brix experiment. In acid conditions, the greater the invert concentration, the greater the drop in pH and the more sucrose loss due to inversion. Actual amounts of sucrose lost were estimated (likely underestimated due to glucose converting to other compounds) by increase in glucose concentration (x 2), with as much as 1.6 % sucrose loss when initial invert concentration was 3%. A direct correlation was observed between sucrose concentration and color development under alkaline conditions and between sucrose concentration and sucrose inversion under acid conditions.

INTRODUCTION

Sugar processing is a complex series of unit operations designed to extract the maximum amount and highest quality of sucrose from sugarcane or sugarbeet. During processing, chemical and physical parameters change (pH, sucrose, temperature, and invert concentrations) in process streams creating color and sucrose loss. The presence of invert sugars is known to be undesirable due to the influence of invert on pH and color development. In cane raw sugar mills and phosphatation refining, invert continues to create sugar processing problems. Beet sugar factories and carbonation refineries today do not have a large invert problem because of the use of carbonatation processes. However, carbonatation processes present an environmental problem, that is what to do with the great amount of carbonate cake produced. There is increasing interest in research activities focusing on alternative processes to replace carbonatation. If new alternative processes do not involve invert destruction, then these processes will also have an invert related processing problem. The specifics of how invert concentrations affect sucrose loss and color development have been discussed in past literature (deBruijn, 1998; Kelly and Brown, 1978; and others). Even under the slightest acidic conditions sucrose is converted to invert sugars through hydrolysis (Edye and Clarke, 1992). The greater the sucrose concentration from juice to syrup, the more inversion occurs, lowering the pH, which induces more sucrose loss to acid hydrolysis. The invert sugars in combination with other process stream constituents (amino acids and phenols) create undesirable color.

Also, invert sugars, particularly fructose, form undesirable caramel color under acid conditions, high molecular weight "caramel-like" colorant under alkaline conditions, and off flavor independently of other juice constituents. A brief summary of potential color reactions is presented in Diagram 1. With sucrose loss, the reducing sugars of primary concern are glucose and fructose. These sugars cannot crystallize out during sucrose crystallization due to their high solubility. Invert concentrations also contribute to the solubility of sucrose and viscosity which affects sugar crystallization. Invert contributes to increased sucrose being carried to molasses (Chen and Chou, 1993), lowering sugar recovery with potentially great adverse economic consequences.

Color Development

- Phenolics - Enzymatic Browning
- Maillard Browning Rxns - Invert + Amino Acid
- Caramel - Thermal degradation of sucrose and reducing sugars
- Invert Degradation Products - Caramels and HMF

Invert Degradation Products

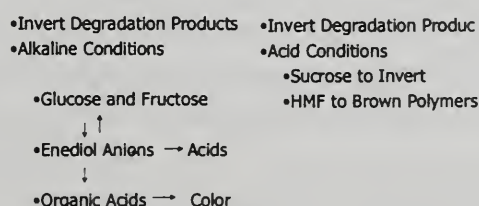


Diagram 1.

These studies were undertaken to further define the role of invert, specifically different invert concentrations, on sucrose loss and color development, independent of Maillard or enzymatic (phenolic) browning reactions. Solutions of 65 Brix (to simulate conditions in mill and refinery evaporators) and 15 Brix (to simulate conditions in clarified juice) were used.

MATERIALS AND METHODS

Materials: 15 Brix and 65 Brix sucrose were spiked with invert(G/F=1)or fructose alone at concentrations of 0 to 4.0% on a solids basis. pH ranged from 6.0 to 9.0. Temperatures used were 80 or 85° C with process simulation times of 0-6 hr.

Analytical Methods:

Invert concentrations were analyzed using a Dionex 500 equipped with a GP50 pump and ED40 PAD with gold cell. The chromatography features included a CarboPac PA1 Column and Guard Column with an isocratic eluent of 150 mM NaOH. All calculations were performed with PeakNet 5.1 software.

Color was analyzed using the Standard ICUMSA Method(ICU).

Dissolved solids and pH were measured using standard electronic instrumentation (refractometer and pH meter, respectively).

RESULTS AND DISCUSSION

Role of invert on pH and color development. Throughout sugar processing in both factory and refinery process streams, pH levels may vary from acidic conditions in juice to alkaline conditions in clarified juice and again more acid conditions in sulfited syrup. Sugars and molasses maintain a pH of 6.0 to 7.0 (Iqbal and Andrews, 2000). Under even slightly acidic conditions, sucrose undergoes inversion through acid hydrolysis (Edye and Clarke, 1992). In beet processing, “Due to the heating and evaporation of water, ammonia and carbon dioxide are eliminated from the juice with the vapor phase, likely influencing the course of the juice pH” (de Bruijn et al 1998). Sucrose is most stable at a pH of 8.2 (Roberts, 1975), while invert sugars are most stable under acid conditions, pH 3-4 (Edye and Clarke, 1992). Due to these opposing conditions, the balance of stabilizing sucrose and invert both becomes complicated.

In this study, the specific effect of pH on color development was examined. Figure 1 compares color formation in a 65 Bx sucrose solution with 0.5% added invert. At pH levels of 6.0 to 8.0, little color was formed even after 6 hours at 85°C. As pH increased, greater amounts of color developed, with a dramatic increase in color development at pH 9.0 after just 2 hours incubation. It is believed that under alkaline conditions, invert sugars undergo condensation and polymerization reactions with ionic

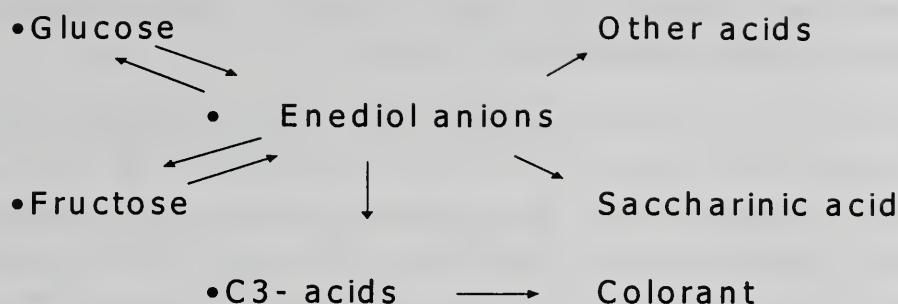


Diagram 2.

intermediates such as 3-carbon compounds (Yu,1998). It is these 3-carbon compounds that then synthesize to high molecular weight “caramel-like”colorants” (Diagram 2).

When the same experiment was conducted with a 15 Brix sucrose solution, similar results were obtained. Figure 2 shows the rapid development of color at pH 9.0 and little or no color development at pH 6.0 and 7.5. When the initial concentration of invert is factored into these process conditions, the data indicated that the greater the initial invert concentration, the more rapidly color develops. In a 65 Brix sucrose solution (pH 9.0), color reached 500 ICU within the first 2 hours of incubation with initial invert concentrations of 2 %. Whereas it took up to 4 hours with the 0.5 and 1.0% added invert (Figure 3). Little or no color was formed in pure sucrose solution with no added invert.

Similarly, in a 15 Brix sucrose solution (pH 9.0), the addition of invert dramatically increased color formation compared with the pure sucrose solution (Figure 4). The effect of sucrose concentration also plays a significant role in the rate of color development, regardless of initial invert level. Figure 5 demonstrates color development eight (8) times greater in 65 Brix sucrose solution than from 15 Brix e.g., at 6 hours incubation a color difference of 680 and 78, respectively. Clearly, any addition of invert into these alkaline process streams will only increase the color formation, even though sucrose itself remains fairly stable under these conditions. These data agree with Madsen *et al.*, (1978) who reported an increase of 1.3 ICUMSA Color per ppm/invert in beet juice streams and de Bruijn (1998), who reported color of 91 ICU in 0.15% invert in raw beet juice; and that when the invert was doubled to 0.3% the color increased an additional 210 IU.

We know that invert is present in all sugar processing streams. If the invert problem is not addressed through carbonatation, the question then becomes how to stabilize sucrose to reduce invert formation and sucrose loss. Under acid conditions, sucrose will undergo acid hydrolysis, with more invert formed and accelerated sucrose loss. Figure 6 looks at the role of pH on invert stabilization. In a 65 Brix sucrose solution, with 2 % added invert, the invert concentration remained between 1.8 and 2.0 % with pH 7.5 and 8.0, however, there was a steady decline in invert level in the more alkaline

conditions with nearly a 20% decrease in total invert at pH 9.0 after just 2 hours. After 6 hours, invert levels began to show a slight increase, especially under progressively more acid conditions. Initial pH 9.0 dropped to 7.7, 6.0, and 5.6 after 2, 4, and 6 hours, respectively. At pH 6.0, there was an approximate 0.2 % increase in invert from acid hydrolysis. With no added invert, sucrose alone underwent inversion under slightly acid conditions (Figure 7), again showing an approximate 0.2 % increase. Sucrose remained stable at pH >7.5 and 9.0.

As previously mentioned, it is well known that reducing sugars will degrade to form carboxylic acids. Figure 8 demonstrates the relationship of invert concentration to the speed and degree of acid formation in 65 Brix sucrose solution. With an initial pH of 9.0 and no added invert, there was little change in pH during the first 4 hours of incubation at 85°C. After 6 hours, the pH dropped from 9.0 to 7.5, but remained in the stable range for sucrose. As invert concentrations were increased, the rate at which the pH dropped increased in direct proportion to the level of added invert. After 6 hr incubation at 0, 0.5, 1.0, and 2.0 % added invert, residual pH for each were 7.5, 6.8, 5.8, and 5.6, respectively. Again, these results indicated that the level of invert had a direct effect on the ability to maintain desired pH in process streams.

Effect of pH and invert on sucrose loss. During thermal processing, especially evaporation, monosaccharides degrade to organic acids creating more acidic conditions. Color formation is due to condensation reactions of color precursors such as hydroxymethylfurfural (HMF) and other color forming compounds. Under these conditions, acid hydrolysis can cause significant loss of sugar (Kelly, 1978). Determining the extent of sugar loss and subsequently to find means to control this loss becomes economically essential. The most accurate measure of sucrose loss would be to analyze for a stable sugar degradation product (Eggleston et al. 1999); however, a reliable one has not yet been determined.

One method suggested to determine sucrose loss (de Bruijn, 1998) was to determine the amount of glucose formed during processing “as a supposed measure of total sugar loss” and multiplied by Factor 2. Although both glucose and fructose will degrade to a variety of by-products (acids, kestoses, color compounds, etc.), glucose is more stable than fructose under process conditions. The level of glucose change and/or the relationship of glucose levels to the amount of fructose present may provide insight into the amount of sucrose loss. The glucose increase may actually underestimate sucrose loss as a result of these further reactions.

When fructose was added to sucrose solutions, as the sole source of invert, increases in glucose became indicative of sucrose inversion. Glucose and fructose concentrations were found to increase nearly equally, so that it was felt that little glucose was lost due to intermediate compounds. Sucrose loss was then calculated according to the deBruijn formula:

$$\text{sucrose loss} = \text{glucose gain} \times 2$$

The effect of invert on sucrose loss became apparent when analyzing solutions of 15 and 65 Brix sucrose solutions at pH 6.0 and with 0-3% added fructose. Figure 9 shows the effect of invert on the destruction of sucrose in 15 Brix solution. With no added fructose, acid hydrolysis was minimal with an increase in glucose from a background of 12 ppm to 500 ppm (.05% solids). It should be noted that analytical grade stock sucrose solutions will contain trace amounts of invert sugars ie 10-40 ppm. However, when 3 % fructose was added, glucose increased to 3500 ppm (0.35% solids). When using the formula, glucose % solids x 2, the estimated loss of sucrose became as high as 0.7% solids in 15 Brix and 3 % added fructose.

In a 65 Brix sucrose solution, sucrose loss was even greater with 3 % fructose addition resulting in an estimated sucrose loss of 1.6 % (Figure 10). All of these estimates were likely underestimates due to an up to 30 % rate of enolization of glucose to other interconversion compounds under process conditions (Wong, 1989). Figures 11,12,13 all demonstrate the effect sucrose concentration had on its own inversion. At levels of invert (as fructose) tested between 0-3%, in all cases sucrose loss was accelerated and significantly increased at 65 Brix compared with 15 Brix. These studies reemphasized the important role invert levels and sucrose concentration have on sucrose loss and color formation.

CONCLUSION

Under the experimental conditions presented here, most color development occurred in solutions at pH 8.5 or greater. This was due to alkaline degradation of invert sugars to "caramel-like" presumed high molecular weight compounds. Fructose was more labile than glucose, although in time both reducing sugars underwent enolization. Under acid conditions, and estimating from increased glucose % solids, the greatest sucrose loss occurred from acid hydrolysis at pH 6.0, the lowest pH tested. In all cases, as invert levels were increased, the degree of color development increased and the greater drop in pH over process time. Also, the greater the sucrose concentration, the greater the sucrose inversion, the greater drop in pH, and the more sucrose inversion due to increased acidity. These studies further emphasized the role of increasing concentrations of invert sugars and process stream sucrose concentrations have on sucrose loss and color development. The color reactions studied here were independent of the important phenolic and Maillard reactions that occur among other process stream components including salts, enzymes, amino acids, invert sugars, etc.

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Figure 1: Effect of pH on Color Development

65 Bx Sucrose, 0.5 % added Invert, 85°C

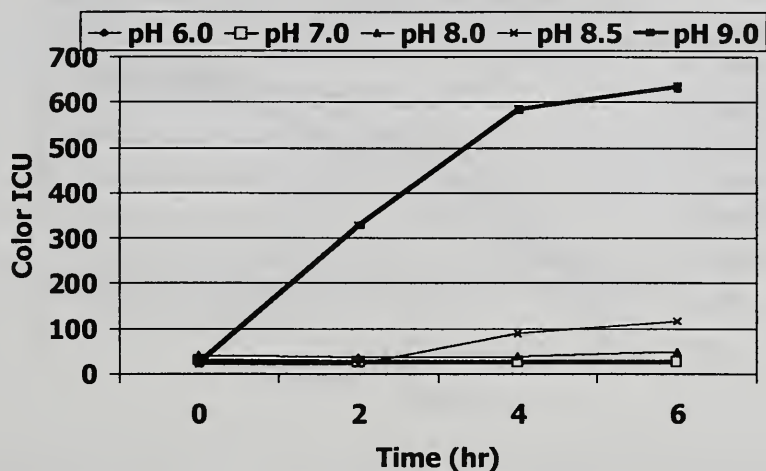


Figure 2: Effect of pH on Color Development

15 Bx Sucrose, 1 % Added Invert, 85°C

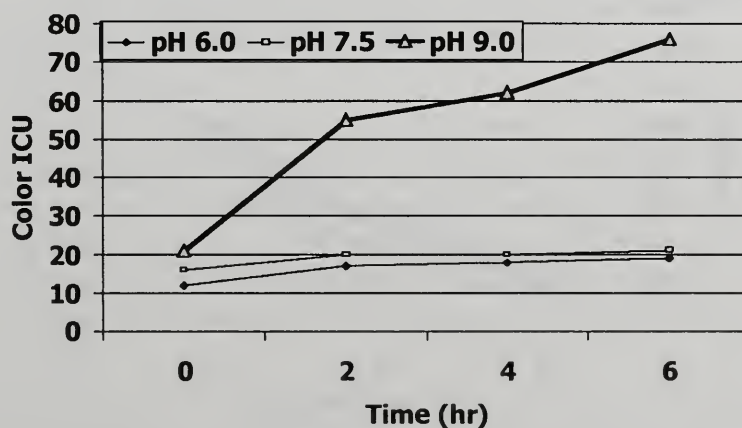


Figure 3: Effect of Invert on Color Development
 65Bx Sucrose, pH 9.0, 85°C

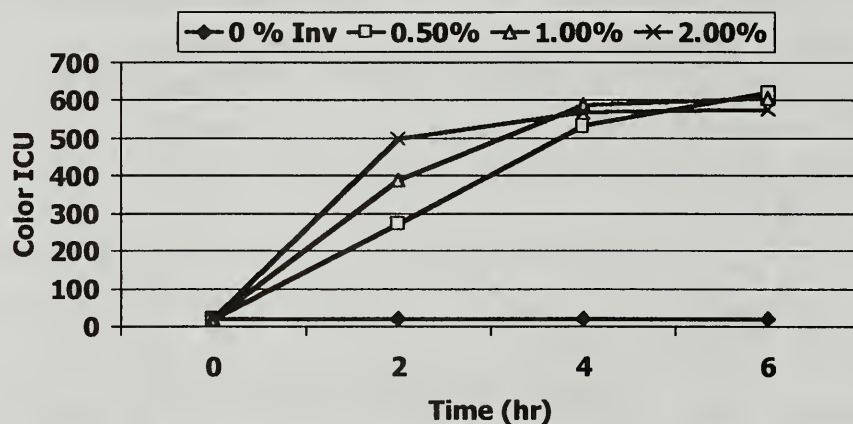


Figure 4: Effect of Invert on Color Development
 15 Bx Sucrose, pH 9.0, 85°C

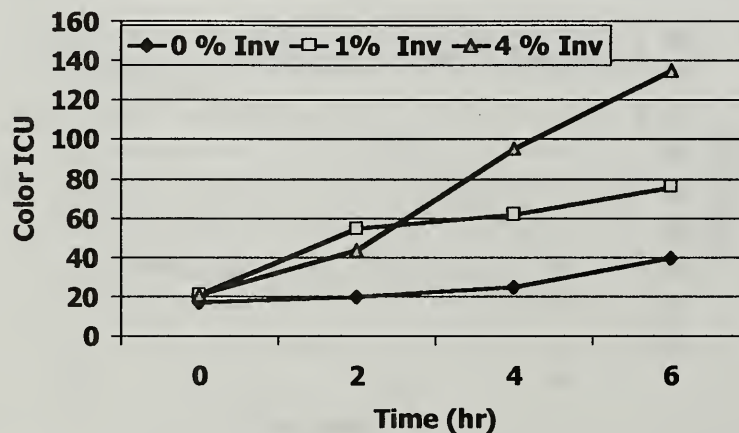


Figure 5: Effect of Sucrose Concentration on Color Development
1 % Added Invert, pH 9.0, 85°C

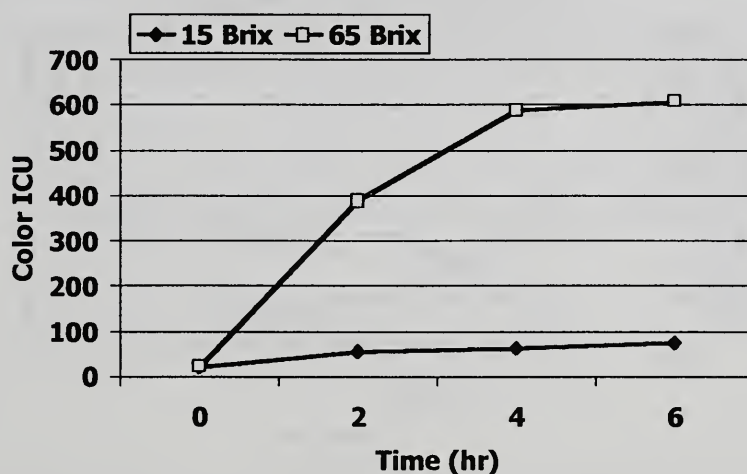


Figure 6: Role of pH on Invert Stabilization
65 Bx Sucrose, 2 % added Invert, 85°C

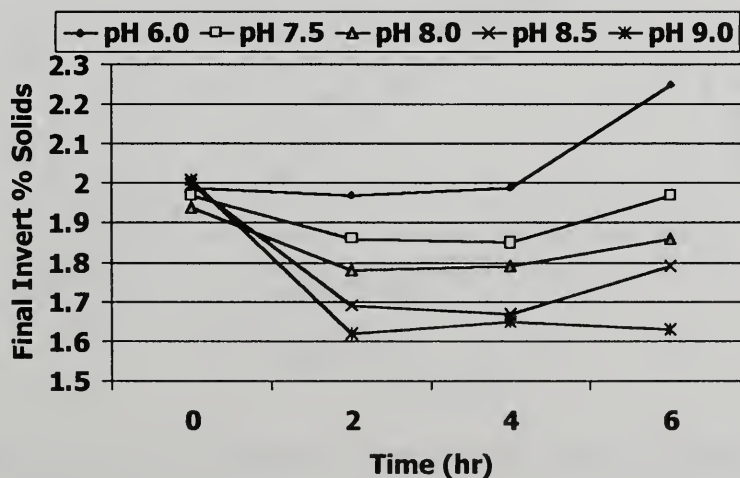


Figure 7: Role of pH on Sucrose Stabilization

65 Bx Sucrose, No added Invert, 85°C

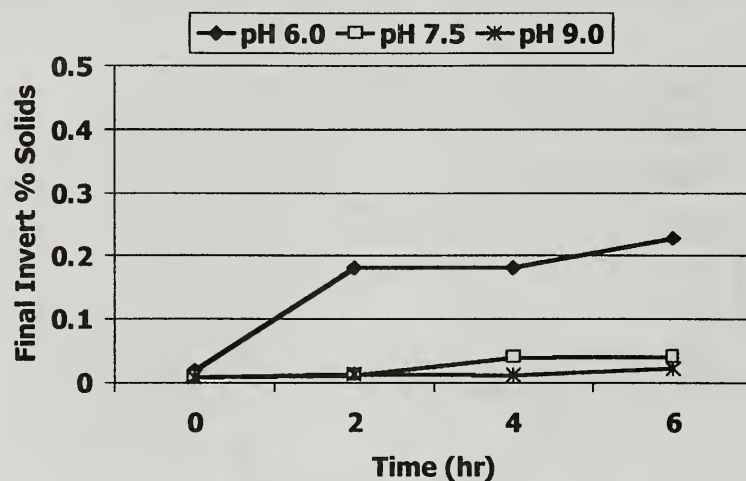


Figure 8: Role of Invert on pH

65 Bx Sucrose, pH 9.0, 85°C

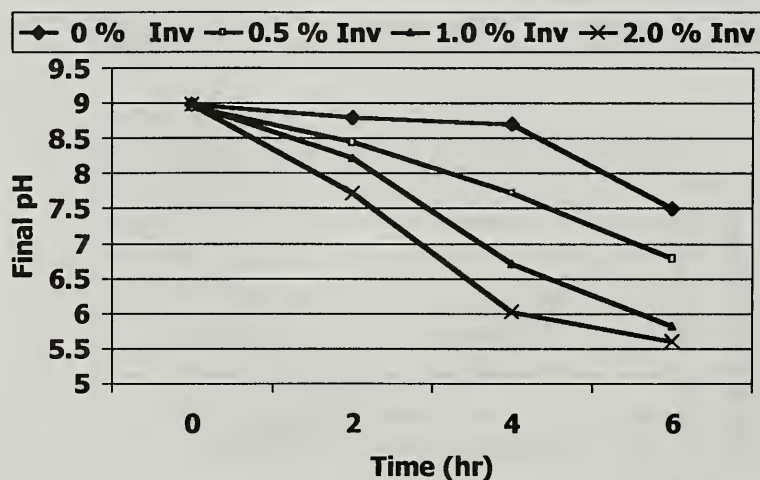


Figure 9: Effect of Invert on Sucrose Degradation

0-3% Fructose, 15Bx Sucrose, pH 6.0, 80°C

•Estimated

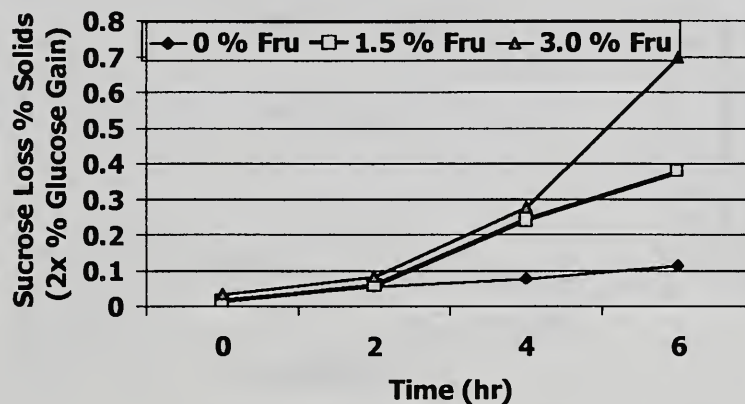


Figure 10: Effect of Invert on Sucrose Degradation

0-3% Fructose, 65Bx Sucrose, pH 6.0, 80°C

•Estimated

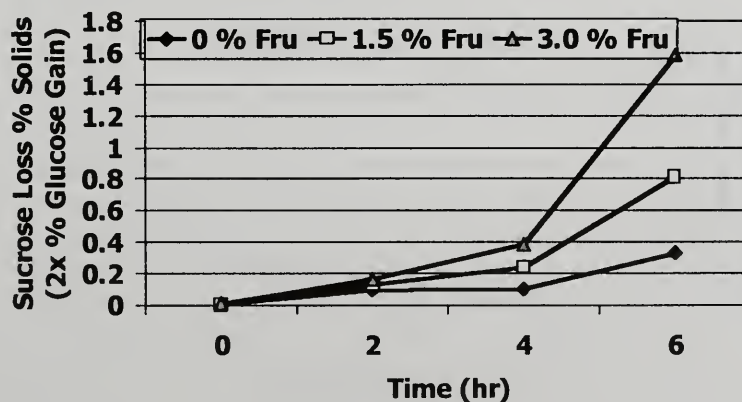


Figure 11: Effect of Sucrose Concentration on Sucrose Loss
No Fructose, 15 & 65Bx Sucrose, pH 6.0, 80°C

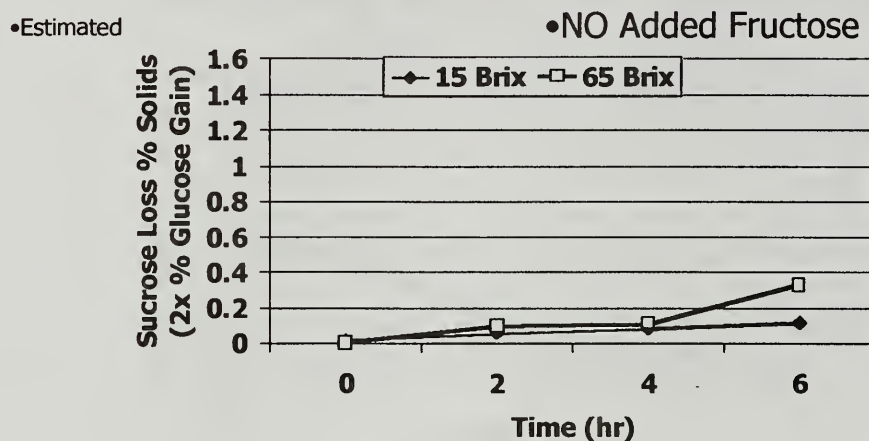


Figure 12: Effect of Sucrose Concentration on Sucrose Loss
1.5 %Fructose, 15 & 65Bx Sucrose, pH 6.0, 80°C

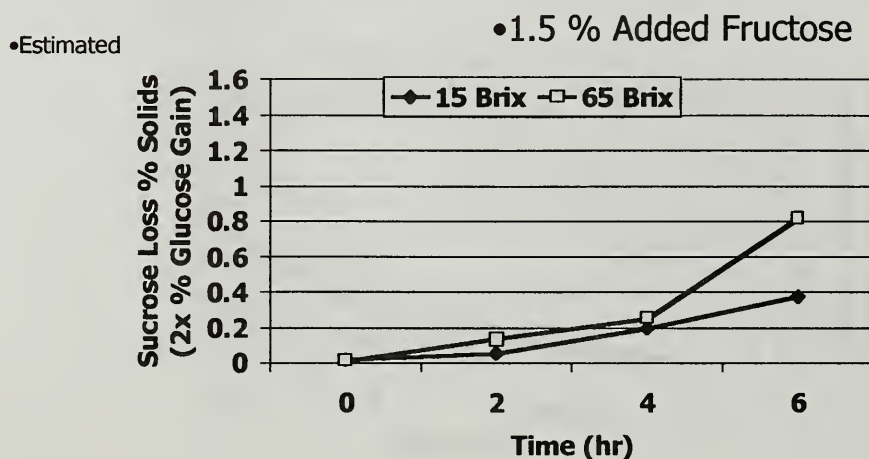
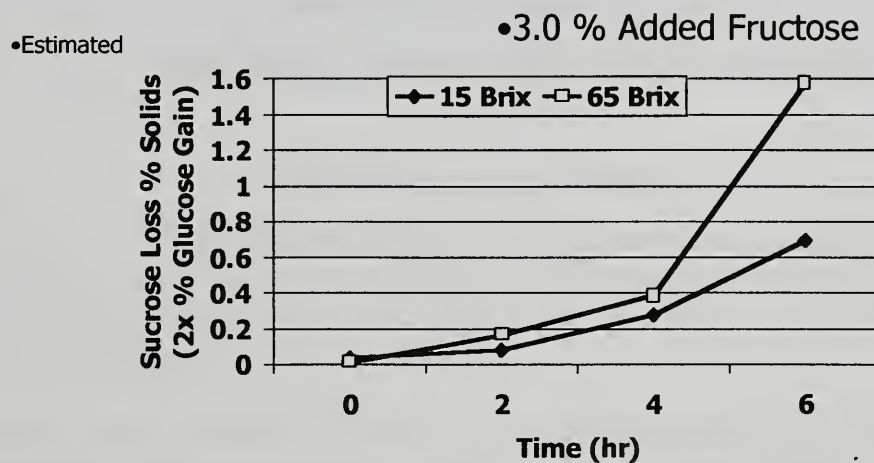


Figure 13: Effect of Sucrose Concentration on Sucrose Loss
3.0 %Fructose, 15 and 65Bx Sucrose, pH 6.0, 80°C



CANE DIFFUSION – AN ENERGY EFFICIENT JUICE EXTRACTION PROCESS

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ABSTRACT

In the cane sugar industry around the world, milling has been used for juice extraction from cane since the inception of the industry. Milling technology has been constantly improved, but never replaced.

With the advent of continuous diffusion technology and its rapid improvement, this process has replaced mills as a means of juice extraction in a few cane sugar plants around the world due to its efficiency, savings in man-power, power consumption, low operating & maintenance costs and better operating flexibility.

INTRODUCTION

India is a major cane sugar producing country with 460 sugar plants and more in the pipeline. Between the late 60's and mid 70's, 13 diffusers were installed at various sugar plants in India. Out of these, within the next few years only one moving screen – percolation type bagasse diffuser remained in operation at The Andhra Sugars Ltd. located at Tanuku, in West Godavari district in the South Indian state of Andhra Pradesh.

Being satisfied with the performance of the first diffuser, our company installed a second moving screen – percolation type bagasse diffuser in 1977. Three decades after the installation of the first diffuser, our company installed a moving screen – percolation type cane diffuser in 1997 at our new sugar plant located at Taduvai in West Godavari District.

These diffusers have worked well for our company for over three decades. Allaying doubts of many in the sugar industry, we are perhaps the only sugar company with diffusers producing

good quality (Table-1) direct consumption plantation white sugar using the double sulphitation process and have consistently had a high recovery.

Table 1: Test Results of 1998 – 99 Sugar Samples

Sample No.	Colour (ICUMSA)	Ash %	Turbidity (Units)	Sulphite (ppm)
1	88	0.024	50	14.4
2	79	0.036	62	13.5
3	88	0.024	60	14.7

DIFFUSION

This is a process in which water or a solution of lower concentration than the juice which the cells contain give up to that water or solution a part or all of the sugar forming the excess of concentration of their juice.

In cane diffusion, sugar extraction from cane is actually effected by rupturing the cane cells and then washing the ruptured cells with water or juice. As sugar extraction depends to a great extent on the proportion of cells ruptured and on the access of the cell contents to the extracting liquid, it is necessary that a preparatory index of at least 90 is achieved to obtain a RME of 97%+.

This process of improved extraction of sugar from cane, unlike in the case of milling, offers several advantages like higher extraction, lower power consumption, lower operating & maintenance costs and better operating flexibility, by merely varying the screen speed and the thickness of the prepared cane mat on this screen. A diffuser could be operated at 20% to 100% of its rated capacity without adversely effecting its efficiency.

There are two alternatives for the use of diffusion at a cane sugar plant:

Bagasse Diffusion:

Cane is passed through one or two sets of mills where 60% of the juice is extracted and the bagasse is then passed through the diffuser.

Cane Diffusion:

Cane is prepared by a fiberiser or a shredder and then passed through the diffuser.

Various types of diffusers are being used by the sugar industry around the world -- the percolation type diffusers are the most widely used in the cane sugar industry. There are two types of percolation diffusers being used -- the fixed screen (drag) type and the moving screen type.

The initial diffusers at most cane sugar plants were bagasse diffusers, where the existing mills were used as primary and dewatering mills. With the advent of improved fiberisers and shredders

that achieve a 90+ preparatory index, cane diffusion has become more popular, doing away with the primary mill and saving on operating costs and energy consumption. With a cane diffuser at a 5000 TCD crush rate, operating at 42 kg/cm².g steam pressure at 420⁰ C, it is possible to export about 2200 KW of electricity more than with a similar capacity milling plant. Annexure IV gives the details. The recovery with a cane diffuser is also about 0.29% higher than that at a similar capacity milling plant.

There are two aspects to be borne in mind when considering the use of diffusion at a Cane Sugar Plant:

- 1) Compared to milling, diffusion requires 2 to 3% more low pressure steam, to heat the prepared cane to the operating temperature of 80⁰ C using vapour bled from the 2nd effect evaporator. This extra 3% steam is used to generate electricity before being used to heat the prepared cane.
- 2) Maceration of 45% on cane is given at the diffuser resulting in a higher load on the boiling house. The diffusion process also results in a higher extraction, which includes non-sugars. The non-sugars are separated at the juice clarifier, using suitable juice clarification equipment.

OPERATION OF A CANE DIFFUSER AT THE TADUVAI SUGAR PLANT

The cane diffusion process is comprised of three major operations:

Cane Preparation :

A heavy duty swing hammer type horizontal fiberiser with 144 hammers (each weighing 17.5 kg) driven by a 2500 BHP steam turbine is being used at the Taduvasi sugar plant, resulting in more cells being ruptured in the shredded cane, exposing the cell contents to the extracting liquid. The fiberiser is also equipped with an auto feed arrangement to have a uniform mat of prepared cane feeding the diffuser.

The power consumed for cane preparation is 1850 HP against an installed HP of 2680.

Juice Extraction :

Juice extraction at this sugar plant is being done using a moving screen – percolation type cane diffuser capable of handling 5000 TCD. This diffuser is a long enclosed, rail wagon like shell, with its bottom made up of a horizontally moving screen running the full length of the diffuser. The moving screen apron is a stainless steel grill. Below the moving screen are 15 recirculation trays, 4 scalding juice tanks and 2 draft juice tanks. At the top, fixed just below the roof of the diffuser are the 15 distributors located to the center of the recirculation trays.

The moving screen moves slowly from the feed end to the discharge end, carrying the prepared cane as a mat of uniform thickness. Compared to milling the imbibition efficiency in diffusion is quite high. Maceration water @ 45% on cane is added on to the moving mat of prepared cane at the discharge-end of the diffuser. This percolates through the mat of prepared cane, which is

copiously irrigated throughout the length of the diffuser through the distributors located at intervals along its length. Along with the maceration water, the dewatering mill juice is also added at the second last compartment at the discharge-end of the diffuser.

Pumps below the recirculation trays pump to the distributors above the preceding tray, the imbibition water that percolates through the mat of prepared cane and collects in the recirculation trays below. The juice moves from the discharge-end to the feed-end causing a counter current extraction. It takes 60 minutes for the prepared cane to traverse the length of the diffuser, while the juice takes 20 minutes. The surplus juice goes to the process house, with the flow being controlled by the level of the juice in the compartment. The draft juice from the diffuser is passed through a DSM Screen before being sent to the process house. This is generally 110 to 115% on cane.

At the discharge-end of the diffuser the bagasse drops on to a rake carrier which carries it to the dewatering mill. To avoid blocking of the prepared cane mat by fine particles, one set of lifting screws is provided after the feed-end and another set before the discharge-end of the diffuser, allowing proper drainage of the high brix juice

The power consumed at the diffuser is 332 HP against an installed HP of 600.

To have a better extraction and to minimise microbial activity in the diffuser the temperature inside the diffuser is maintained at around 80⁰ C. To maintain this temperature, a fully automatic controlled 1st vapour steam injection is provided in the diffuser. To raise the temperature of the prepared cane to the operating temperature, the juice from the scalding compartment is heated in two multipass vertical juice heaters and spread over the prepared cane mat at the feed-end of the diffuser.

Normally at this stage cane juice is at 5.2 to 5.4 pH. Automatic pH control is provided, by adding milk of lime to maintain the pH between 5.8 to 6.0. As the temperature of the juice in the diffuser is maintained at around 80⁰ C, inversion is avoided. Annexure-I shows the pH and brix of the juice at the various compartments of the diffuser at the Taduvai sugar plant. From Annexure - I it will be seen that the Reducing Sugars/100 Brix is constant from the feed-end to the discharge-end of the diffuser, indicating that there has been no inversion inside the diffuser.

The filtrate collected at the rotary vacuum filter is added in the diffuser at a location where the brix of the diffuser juice and the filtrate are the same. The mat of prepared cane in the diffuser acts as a filter, removing the mud particles in the filtrate and the suspended particles from the diffuser juice. Due to this, the recirculation of the filtrate is avoided and there is a significant improvement in the clarity of the juice. The addition of the filtrate in the diffuser has not effected the boiler in any way.

Table 2: The Cane Diffuser Performance Record as on 31 Dec 1999:

	12 Noon to 1 PM	1 PM to 2 PM	2 PM to 3 PM	3 PM to 4 PM	4 PM to 5 PM	5 PM to 6 PM	6 P.M to 7 PM	7P.M to 8PM
Crush rate , TCH	175	160	170	160	161	160	175	177
Cane Carrier speed Set point, m/min	7.26	7.26	7.26	7.26	7.26	7.26	7.26	7.26
Fiberiser turbine chest pressure set point, kg/cm ² g	21	18	18	18	18	18	20	20
Diffuser screen speed, m/min	0.656	0.656	0.656	0.656	0.656	0.656	0.656	0.656
Diffuser mat thickness, m	1.40	1.50	1.50	1.50	1.50	1.50	1.55	1.55
Scalding Juice flow No.1, m ³ /Hr.	180	170	178	170	172	175	180	180
Scalding Juice flow No.2, m ³ /Hr.	160	162	160	156	155	160	162	160
Draft Juice flow, m ³ /Hr.	185	172	181	179	177	177	185	189
Imbibition water Flow, m ³ /Hr.	80	78	78	78	78	78	78	80
Imbibition water temperature, °C.	76	74	76	92	90	86	88	90
Press Juice Brix		1.38	1.20	1.62	1.38	..	1.47	..
Bagasse Pol		1.26		1.24		1.24	1.24	1.22
Bagasse Moisture, %		50.5					50.5	50.5

Dewatering of Bagasse:

The moisture content of the bagasse discharged from the diffuser is around 80%. To use this bagasse as fuel for the boiler, it is passed through a 39" x 78" mill with a TRPF and driven by a hydraulic drive. The moisture percentage of the bagasse at the outlet of the dewatering mill is around 50 to 50.5%.

The power consumed at the dewatering mill is 540 HP against an installed HP of 1050.

ADVANTAGES OF CANE DIFFUSION (considering a 5000 TCD Sugar Plant):**Flexibility :**

The diffuser can be operated without any change in equipment and without any loss of efficiency from 20% to 100% of its rated capacity, by merely varying the bed height and the screen speed.

Lower Foundation & Building Costs :

The foundation and building costs at a milling plant are higher than that at a similar capacity cane diffusion plant, as more equipment is used needed for juice extraction at a milling plant than at a cane diffusion plant.

The foundation cost for the juice extraction section for this capacity plant in India is:

Description	US \$	
In a milling plant the foundation cost for 4 sets of mills, 4 intermediate carriers and 4 pumps @ \$35,500/set		142,000
In a cane diffusion plant the foundation cost for:		
Diffuser	4,700	
One dewatering mill	35,300	
Total Cost		40,000

While the diffuser can be installed outdoors, the milling tandem requires a complete roof cover. This is an additional cost in the case of a milling plant.

Lower Power Consumption:

The installed HP at a milling plant (4 sets of mills) and a cane diffusion plant is:

Description	Installed HP	
	Milling	Cane diffusion
Cane preparation	2465	2680
Juice extraction	3200	2040
Total HP	5665	4720

Annexure – II gives the details of the installed power. With a diffuser a RME of 97% + is achieved. To achieve this RME at a milling plant, two more sets of mills will be needed, increasing the installed power by another 1500 HP.

Operation And Maintenance Costs :

The operation and maintenance costs at a milling plant and at a cane diffusion plant are:

Description	US\$
Milling	54,000
Cane Diffusion	24,000

Annexure –III gives the details.

Lubricants :

The cost of lubricants at a milling plant is comparatively higher than that at a cane diffusion plant

Description	Cost of lubricants for 150 days of operation, US \$
Milling	10,600
Cane Diffusion	2,900

Clarification and Filtration:

The mat of prepared cane in a diffuser acts as a filter, removing sand, soil and other suspended matter from the juice. The filter cake % cane is 1.0 in the case of diffusion, so the losses in the filter cake are also less.

The under flow from the clarifier can be added in the Diffuser, reducing the recirculation of non-sugars at the clarifier.

Unknown Losses:

Diffusion takes place in a closed equipment, at a temperature where there is no microbial activity, so the loss due to microbial activity is nil. While milling is done in the open, at a low temperature, leading to microbial activity, where losses above 0.1% is common.

Exportable Electricity:

A 5000 TCD cane sugar plant, with a cane diffuser, can export about 2200 KW more power than with a milling plant of the same capacity. Annexure – IV gives the details.

With a cane diffusion plant, at a crush rate of 3500 TCD the Taduvai Sugar plant is exporting 3.2 to 3.4 M.W. after meeting the power requirement in the plant during the season. During the off-season 4.4 M.W are exported using a back pressure turbine and an evaporator body as a condenser.

Higher Overall Recovery:

	Milling (RME of 95%)	Cane Diffusion (RME of 97%)
Pol in Cane, %	13	13
Pol in mixed juice, %Cane	12.35	12.61
Pol in Bagasse, % Cane	0.665	0.39
Pol in Filter Cake, % Cane	0.06 (2.3% F.C)	0.025 (1% F.C)
Pol in Molasses, % Cane	1.15(4% of Molasses)	1.3 (4.5% of Molasses)
Miscellaneous unknown	0.19	0.04
Recovery	10.95	11.245

This is how the recovery at a cane diffusion plant is 0.295% higher than that at a similar capacity milling plant.

CONCLUSION

Cane diffusion is better than milling for juice extraction due to higher extraction, lower power consumption, lower operating and maintenance costs and better operating flexibility

The use of cane diffusion is more advantageous for sugar plants considering co-generation for the export of power to generate an additional income in power starved locations.

ACKNOWLEDGEMENT:

The authors express their thanks to the management of The Andhra Sugars Limited for their permission to present this paper. We are also thankful to our Joint Managing Director (Sugar), Sri Mullapudi Narendranath for reading through our paper and writing it in this form.

**BRIX, pH AND TEMPERATURE AT THE VARIOUS COMPARTMENTS OF
THE CANE DIFFUSER AT TADUVAI**

Compartment No.	Brix	pH	Temperature
1	1.14	5.96	76
2	1.44	5.94	80
3	1.84	5.90	81
4	2.21	5.77	84
5	2.44	5.74	85
6	3.11	5.75	82
7	3.48	5.63	81
8	4.04	5.64	81
9	5.04	5.58	81
10	5.84	5.59	82
11	7.04	5.54	82
12	8.24	5.55	84
13	9.41	5.50	83
* SJ 4(2)	11.51	5.57	86
1	12.94	5.63	94
** Dr. Juice	15.34	5.45	71

Reducing Sugars of Diffuser Juice per 100 Brix is 5.29

Reducing Sugars of Lab mill juice per 100 Brix is 5.19

* S.J = Scalding Juice

** Dr.Juice = Draft Juice.

INSTALLED POWER**CANE PREPARATION:**

	Milling (RME of 95%) HP	Cane Diffusion (RME of 97%) HP
Cane Chopper	240	75
Cane Cutter	500	
Fiberiser	1600	2500
Cane Carrier	75	75
Rake Carrier	50	30
Total HP	2465	2680

JUICE EXTRACTION:

Milling:	H.P
* 4 sets of Mills 4 x 750	3000 (4500 HP for 6 sets of Mills)
4 Pumps 4 x 20	80
4 Carriers 4 x 30	120
Total HP	3200
Cane Diffusion :	
Diffuser	600
Belt Conveyor	30
Rake Carrier	30
Press Juice Pump	30
Dewatering Mill	1350
Total HP	2040

* A diffuser achieves a RME of 97%+. To achieve this RME at a milling plant, six sets of mills are required, increasing the installed power by another 1500 HP.

MAINTENANCE COST

MILLING		CANE DIFFUSION	
Particulars	Amount in US \$	Particulars	Amount in US \$
Out of 12 rollers, 4 reshellings / yr.	11,295	Out of 3 rollers, 1 reshellings / yr.	2,825
For 4 Nos.trash plates @ \$920 / piece	3,680	For 1 trash plate @ \$920 / piece	920
For mill rollers, arcing @ US \$ 470 per mill	1,880	For mill rollers arcing @ US \$ 470 per mill	470
Out of 8 Nos. mill scrapers, 4Nos. per year @ US\$ 280 / piece	1,120	Out of 2 Nos. mill scrapers, 1No. per year @ US\$ 280 / piece	280
Out of 12 Nos. mill roller pinions, 4 Nos. per year @ US \$ 120	480	For 3 Nos. mill roller pinions 1 Nos. per year @ US \$ 120 / piece	120
For maintenance of pumps 8 Nos. @ US \$ 70 / pump	560	For maintenance of pumps 2 Nos. @ US \$ 70 / pump	140
For maintenance of inner carriers 4 Nos. @ US \$ 1182 for 3 years	1,576	For maintenance of inner carriers 1 Nos.@ US \$ 1182 for 3 years	394
Maintenance cost for mill bearings 32 Nos. @ US \$ 470 for 5 years	3,010	Maintenance cost for mill bearings 8 Nos. US \$ 470 for 6 years	627
Spares for prime movers and R / gears 4 Nos @ US \$ 2355 / piece	9,420	Spares for prime movers and R / gears 1 Nos @ US \$2355 / piece	2,355
Cost of lubricants for mill bearings 12 lit / 8 hrs. / mill @ US \$ 0.35 per lit. For 150 days of crushing for 4 sets of mills.	7,560	Cost of lubricants for mill bearings 12 lit / 8 hrs. / mill @ US \$ 0.35 per lit. For 150 days of crushing for 1 set of mill.	1,890
Cost of lubricants for prime mover & R / gears 800 lit / mill @ US \$ 1.90 for 4 sets of mills for 2 years	3,040	Cost of lubricants for prime mover & R / gears 800 lit / mill @ US \$ 1.90 for one set of mill for 2 years	760
Nil		Cost of lubricants for a diffuser for 150 days of operation	280
Labour cost for off-season overhauling of 4 sets of mills & inter carriers etc.2880 mandays @ US \$ 3.5 / manday	10,080	Labour cost for off-season overhauling of one set of mills 720 mandays @ US \$ 3.5 / manday	2,520
Nil		Labour cost for overhauling of a diffuser 1260 mandays @ US \$ 3.5 / manday	4,410

ANNEXURE – III (contd..)

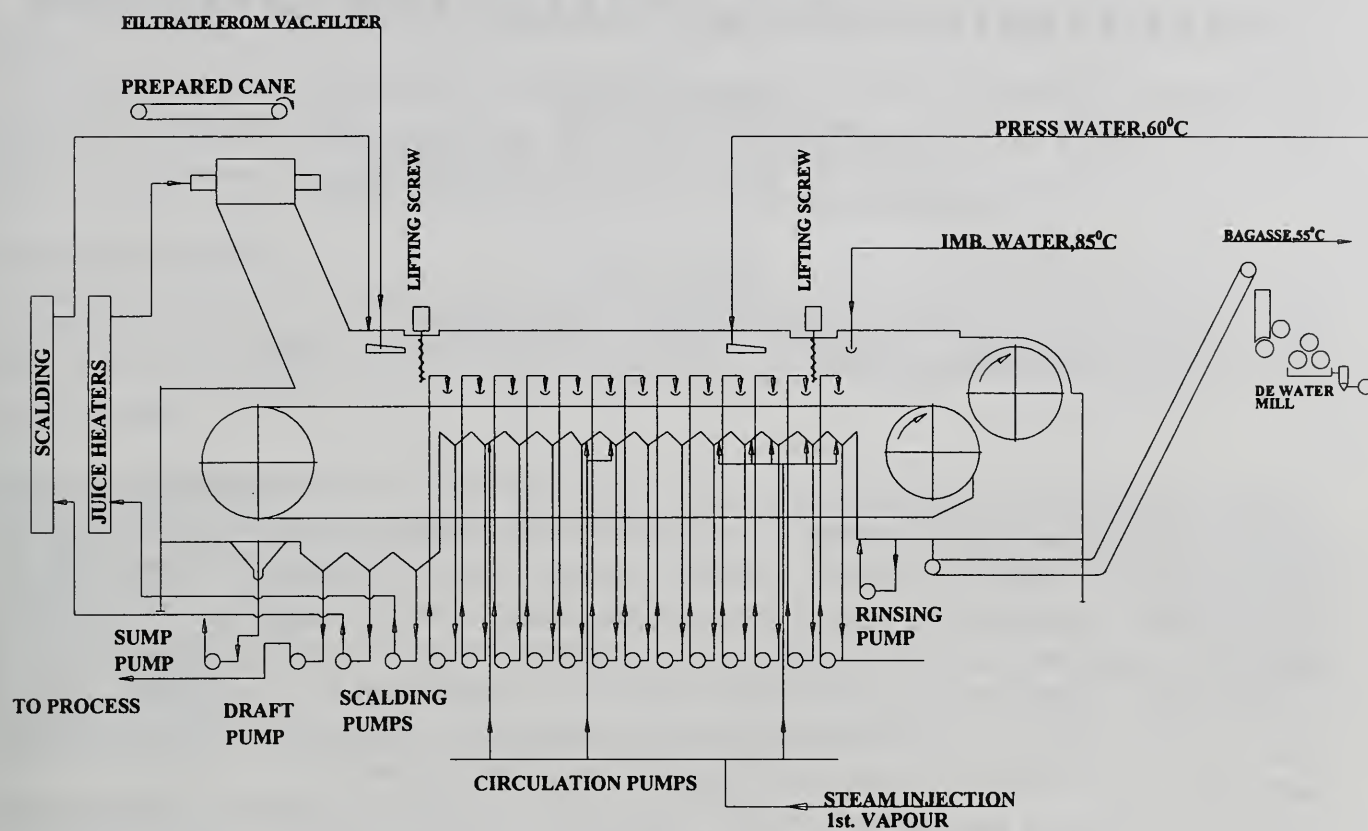
MILLING		CANE DIFFUSION	
Particulars	Amount in US \$	Particulars	Amount in US \$
Nil		Spares & off-season main- tenance cost for a diffuser: runner flats 2 MT @ US \$ 940- 2 yrs life; main chain @ US \$ 50 / x244 links for 6 yrs. Life	2,973
Nil		Spares for lifting screws 4 yrs life 8 Nos @ US \$ 120	240
Nil		Spares for circulation and scalding pumps – 23 nos. @ US \$50 / pump	1,150
Painting cost	235	Painting cost	1,200
Total	53,936		23,554
Rounded off to	54,000		24,000

**COMPARISON OF ENERGY REQUIREMENTS AT A MILLING
AND A CANE DIFFUSION PLANT**

Description	Milling	Cane Diffusion
Cane Crush rate, TCD	5000	5000
Bagasse Production, mt / hr	67.34 (29.28%)	70.15 (30.5%)
Bagasse used for filter cake, mt / hr	2.3 (3%)	0.77 (1%)
Bagasse available, mt / hr	65.06	69.38
Exhaust steam, % cane	45	48
Exhaust steam requirement, mt / hr	103.5	110.4
De-super heated water required, mt / hr	3.39	3.62
High pressure steam required to produce the required exhaust, mt / hr	100.11	106.78
HP steam required for miscellaneous use, mt / hr (3.5% on cane)	8.05	8.05
Total high pressure steam to be generated, mt / hr	108.16	114.83
Power generated while producing the required exhaust, KW	12510	13350
Power used for cane preparation, KW	1740	1896
Power used for juice extraction, KW	2005	1163
Power used for other plant load, KW	4216	4141
Total power utilised, KW	7961	7200
Surplus Power, KW	4549	6150
Bagasse Consumed, mt / hr	48.5	51.5
Surplus Bagasse, mt / hr	16.56	17.88
Steam equivalent to surplus bagasse, mt / hr	36.92	39.87
Power generated from the surplus bagasse with a condensing turbine, KW	7384	7974
Net exportable power, KW	11933	14124

A sugar plant with a diffuser exports about 2200 KW more power than with a milling plant of the same capacity.

CANE DIFFUSION – AN ENERGY EFFICIENT JUICE EXTRACTION PROCESS



EFFECT OF CLARIFICATION OF SUGAR SOLUTION BY ULTRAFILTRATION ON CRYSTALLIZATION OF SUCROSE

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Sugar crystallization is a principal process in sugar processing, and sugar recovery and quality through crystallization greatly depend on the kind and the amount of impurities contained in the sugar solution. It is known that invert sugar and inorganic salts in the sugar solution hinder the crystallization of sucrose and increase the volume of molasses. In general, most impurities enhance the solubility of sucrose at higher concentration and at higher temperature; the impurities that increase the solubility are referred to as melassigenic^{1,2)}. Different kinds of impurities have different levels of influence on the formation of molasses¹⁻⁴⁾ and "melassigenic coefficients" of a number of individual impurities were determined by Z. A. Siline^{1,2)}. Many formulas are in use for calculating "available sugar" under consideration of pol or purity in cane sugar factories^{2b,5b-7)} and in beet sugar factories^{8-9d)}. In the refinery, "rendement" which is the formula for calculating the yield of refined sugar under consideration of pol and contents of invert sugar and ash is used^{5a,9b-11)}. Thus the influence of the low molecular weight impurities on the crystallization of sucrose has been discussed. However, it has been hardly been reported how high molecular weight impurities (HM) in the sugar solution affect on the crystallization.

Ultrafiltration (UF), electrodialysis (ED) and chromatographic separation (CS) are rather modern techniques in the sugar industry and several companies adopted these¹²⁻¹⁶⁾. By these techniques industrial sugar solution can be clarified more effectively than by the traditional methods¹⁷⁻²⁷⁾. Through ED^{12,20)} or CS¹⁵⁻¹⁹⁾, the purity in the sugar solution is enhanced and the yield of sugar is increased. Through UF, HM and turbid substances are exhaustively eliminated^{21,22)} but the purity is only a little increased because the content of HM in sugar solution is low. It is reported that light color sugar is recovered from the sugar solution clarified through UF^{23,24)}.

UF is validly applicable to eliminate HM, while the elimination through the traditional clarification is not sufficient. The effect of clarification of sugar solution by UF on crystallizing sucrose was studied and also it was discussed how UF improves the physical properties of the sugar solution which has an influence on handling of pan boiling.

MATERIALS AND METHOS

1. *Sample sugars*

Sugars tested were an Australian raw sugar (Raw Sugar A), an Australian high pol sugar (HP Sugar A) and a Thailand high pol sugar (HP Sugar T). Composition of these sugars is listed in Table 1. In Japan, raw sugar having higher polarization than 98 pol is called "high pol sugar". Another raw sugar (Raw Sugar B) was used for preparation of HM.

2. *UF*

UF experiment was performed at an applied pressure of 2 atm using an MC-4 type UF cell (Bio-Engineering Co., Tokyo) equipped with YM-100 membrane (Amicon, Danvers, MA) with molecular weight cut-off of 100,000.

3. *Preparation of HM*

Raw Sugar B solution was subjected to diafiltration through YM-100 membrane until no sugar became detected in the permeate. The retentate, which contained high molecular weight substances in Raw Sugar B was evaporated to dryness. The amount of solid is represented as the amount of HM.

4. *Decolorization test*

Granular carbon (from coconut shell, 32-60 meshes, Nacalai Tesque Inc., Kyoto) and anion exchange resin (Amberlite IRA-400 Cl-form, Organo Co. Ltd., Tokyo) were used for decolorization of sugar solution. Adsorption isotherm was prepared on the basis of decolorization test in which 1 g of each adsorbent was added to 20 ml of the sugar solution and color after decorization at 60°C for 24 h was determined. The color value was represented as absorbance at 420 nm through 1 cm thickness of the sugar solution.

5. *Determination of polysaccharides*

A method according to Shinohara³⁰⁾ was modified. To the sugar solution adjusted to Bx 50°, 5 volumes of acidified ethanol (5 parts of 95% ethanol + 1 part of 1:1 HCl) were added, mixed thoroughly and allowed to stand for 1 hour. Turbidity was measured as absorbance of the solution at 720 nm and polysaccharides were determined from a calibration curve prepared using Dextran T 2000 (Pharmacia Biotech Ltd, Buckinghamshire).

6. *Measurement of physical properties of sugar solution*

Concentration of the sugar solution tested was adjusted to Bx 65°. Viscosity of the sugar solution was measured at 25°C with a B-type viscometer (Tokyo Keiki Co., Tokyo) and surface tension was measured at 20°C with a Du Noüy type tension meter (Rigosha Co., Tokyo).

7. *Crystallization test*

One hundred grams of sugar solution of 1.1 supersaturation was seeded with 5 g of sucrose crystals (mesh size, 35-45). The crystals were grown in a sealed flask at 22°C under shaking. The sugar concentration of the mother liquor was determined after the crystallization.

RESULTS AND DISCUSSIN

1. Clarification of sugar solution by UF

1.1. Flux.

The sample sugar solutions were ultrafiltered at 2 atm. The permeation fluxes declined steeply for the initial 30 min after beginning UF, and then more slowly thereafter. Permeation flux in UF of Raw sugar A solution at different concentrations is shown in Figure 1. The permeation flux was measured at 30 min after beginning UF. The mass flux of solids (J_M kg/m²h) was obtained by multiplying the permeation flux (J_V l/m²h) by the solids content (C_S °Bx) and by the density of the solution (d kg/l), using the following equation.

$$J_M = J_V d C_S / 100$$

The mass flux is also shown in Figure 1. The mass flux was the greatest at Bx 20-30° and the result was consistent with that obtained early in UF of middle juices²³⁾. The permeation fluxes in UF of Bx 50° Raw sugar A solution at 40, 50 and 60°C were 5.8, 8.0 and 8.8 l/m²h, respectively. The permeation fluxes became greater with a temperature increase. The increase of the flux can be ascribed to the decline of viscosity with the rise in temperature. The flux is influenced by concentration polarization formed on the UF membrane, which is controlled by mass transfer coefficient. The mass transfer coefficient (k) in a stirred vessel is represented by the following equation³¹⁾.

$$k = (D/r) 0.0443 (v_K/D)^{0.33} (w r^2/v_K)^{0.75}$$

with D = diffusion coefficient, r = cell radius, w = stirrer speed, v_K = kinetic viscosity ($v_K = v_S/d$), v_S = viscosity and d = density. Because the equation contains viscosity, it is clear that the flux is influenced by the viscosity.

The mass fluxes in UF of Bx 50° solution of Raw Sugar A, HP Sugar A, HP Sugar T and sucrose were 7.8, 9.9, 7.9 and 26.0 kg/m²h, respectively. Although the purity of HP Sugar T was the highest (see Table 1), the mass flux was smaller than that for HP Sugar A and was almost the same as that for Raw Sugar A. It seems that the cause of the small flux depended on the amount of the turbid substances contained in the sample sugars.

1.2. Elimination of color and polysaccharides.

Through UF of Raw Sugar A, HP Sugar A and HP Sugar T, the color values diminished by 35, 33 and 37%, respectively. High molecular weight color can be eliminated by UF but low molecular weight color cannot be eliminated.

The polysaccharides were exhaustively eliminated through UF. It is reported that the polysaccharides are found in granulated cane sugar and may cause it to form floc in carbonated beverages³²⁻³⁴⁾. It seems that UF for sugar solution is an effective means to control this trouble.

1.3. *Effect of UF on decolorization with adsorbents.*

Raw Sugar A and the UF permeate were decolorized with granular carbon and anion exchange resin. The adsorption isotherms of color of these samples are shown in Figure 2. When strong adsorption occurs, the graph of the isotherm is drawn at left and upper side of the section paper. Figure 2 shows the isotherm curves of UF permeates are drawn at this part. Consequently, the color of UF permeate was more easily decolorized with the granular carbon and the anion exchange resin than the original sugar solution before UF.

2. *Effect of UF on crystallization*

Sample sugar solutions of Bx 50° were ultrafiltered. The permeate and the retentate were concentrated to a supersaturation of 1.1. To the supersaturated solutions were added seeds and after crystallization the sugar concentration in the mother liquor was determined. The original sugar solution before UF was also tested. The results are shown in Table 2. Sugar concentrations (Bx) in the mother liquors after crystallization from the permeates of the three sample sugar solutions were smaller by 0.2-0.3° than those from the respective original sugar solutions, and those from the retentates were larger by 0.1-0.2°. The fact implies that a larger amount of sucrose can be recovered from the permeate by crystallization. The brix in the mother liquor after crystallization from the UF permeate (which does not contain HM) of Raw Sugar A (purity of 98.3) was smaller than that from HP Sugar A (which contains HM and had a purity of 99.3) before UF. This observation suggests that HM might hinder the crystallization of sucrose.

3. *Influence of HM on crystallization*

In order to examine the influence of HM on crystallization of sucrose, a variety of model sugar solutions which contained HM as well as invert sugar (IS) and potassium chloride (KCl) were prepared. The model sugar solutions were subjected to the crystallization test.

3.1. *Hindering effect of HM on crystallization.*

Different amounts of HM were added to sucrose and the mixtures were dissolved in distilled water. The results of the crystallization tests using the model sugar solutions are shown in Table 3. In the table, the figures in the parentheses following "HM" represent the weight of HM added to 100 g sucrose. Namely, "Sucrose + HM (0.1)" means that 0.1 g of HM is added to 100 g sucrose and the mixture is dissolved in distilled water. As shown in Table 3, The sugar concentrations after crystallization from the model sugar solutions were larger as larger amounts of HM were added. It is clear that HM hindered the crystallization of sucrose.

3.2. *Comparison of hindering effects of HM and IS on crystallization.*

It is well known that invert sugar (IS) hinders the crystallization of sucrose and is a melassigenic substance¹⁻²⁾. We compared the hindering effect of IS with that of HM. The results of crystallization tests using the model sugar solutions which contained HM and/or IS are shown in Table 4. In the table, the results for Raw sugar B are also shown. Although the purity of Sucrose + HM (0.2) was higher than that of Sucrose + IS (1.73), the sugar concentration after crystallization of both the sugar solutions were the same. Therefore, it is clear that HM hindered more heavily the crystallization of sucrose than IS. This fact is confirmed by the observations

that the sugar concentration after crystallization of Raw sugar B solution which originally contained HM was higher than that of Sucrose + IS (1.73) with the same purity (98.27), and the sugar concentration after crystallization became larger when a small amount of HM (0.1) was added to Sucrose + IS (1.73).

3.3. *Comparison of hindering effects of HM and KCl on crystallization.*

Potassium chloride (KCl) is also known as a melassigenic substance ¹⁻²⁾ and then it was adopted as representative of ash in raw sugar. The results of crystallization tests for the model sugar solutions which contained HM, IS and/or KCl are shown in Table 5. The IS content (0.39%) and the ash content (0.47%) in Sucrose + IS (0.39) + KCl (0.47) in Table 2 were the same contents as Raw sugar A in Table 1, respectively. The sugar concentrations after crystallization for Sucrose + IS (0.39) + KCl (0.47) and Sucrose + HM (0.2) were the same although the purity of Sucrose + HM (0.2) was higher. The sugar concentration after crystallization for Sucrose + IS (0.39) + KCl (0.47) was smaller than that for Sucrose + IS (0.39) + KCl (0.47) + HM (0.1) added small amount of HM. These observations suggest that HM hindered more heavily the crystallization of sucrose than potassium chloride.

Consequently, it is concluded that HM hindered more heavily the crystallization of sucrose than invert sugar and potassium chloride.

4. *Effect of UF on physical properties of sugar solutions*

Viscosity and surface tension of Raw Sugar A solution and its UF permeate are shown in Table 6 and those of granulated sugar solutions are also shown. The viscosity of the permeate was smaller than Raw Sugar A and was rather close to that of the granular sugar solution. It is sufficiently revealed that the decrease in viscosity causes better circulation of the massecuite in boiling pan and crystallization of sucrose is promoted. The surface tension of Raw Sugar A solution was enhanced through the UF. This observation means that surface active substances which can cause foaming during pan boiling were eliminated. Thus, the physical properties (viscosity and surface tension) of sugar solutions are evidently improved by UF, and it is expected that the handling of pan boiling may become easier and the boiling time may be shortened.

CONCLUSIONS

- 1) The polysaccharides in sample raw sugars were exhaustively eliminated by UF. The color of the raw sugar solutions decreased by about 30% through UF, and the permeate was more easily decolorized with granular carbon and anion exchange resin.

- 2) Crystallization of sucrose was improved in the UF permeate of Raw sugar A solution. High molecular weight impurities (HM) hindered sucrose crystallization; the hindering effect of HM was larger than that of invert sugar and potassium chloride.
- 3) Viscosity of Raw Sugar A solution was decreased through UF and the surface tension was increased. These observations suggest that the handling of pan boiling may become easier.

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Table 1. Composition of sample sugars

	Sample sugar * ¹		
	Raw Sugar A	HP Sugar A	HP Sugar T
Moisture (%)	0.38	0.22	0.05
Pol	97.9	99.1	99.7
Invert sugar (%)	0.39	0.36	0.17
Turbidity * ²	38.6	23.4	46.3
Color unit (IU) * ³	3087	2856	874
Polysaccharides (ppm) * ⁴	1100	620	540
Ash (%)	0.47	0.26	0.09
Purity	98.3	99.3	99.7

*¹ Raw Sugar A: Raw sugar from Australia, HP Sugar A: High pol sugar from Australia, HP Sugar T: High pol sugar from Thailand.

*² Turbidity was determined by a method described in the literature ^{9c,28}).

*³ "IU" is ICUMSA unit ^{9a,29}).

*⁴ Polysaccharides are substances which are insoluble in acidified ethanol solution.

Table 2. Crystallization test of sample sugar solutions before and after UF

Sample sugar	Concentration in mother liquor after crystallization		
	Original solution	Permeate	Retentate
Raw Sugar A	68.6° Bx	68.3° Bx	68.8° Bx
HP Sugar A	68.4° Bx	68.2° Bx	68.6° Bx
HP Sugar T	68.2° Bx	68.0° Bx	68.3° Bx

The permeate and the retentate after UF were concentrated to a supersaturation of 1.1. To the supersaturated solutions were added seeds and the sugar concentration in the mother liquor after crystallization was determined.

Table 3. Effect of HM on hindering of crystallization of sucrose

Model sugar solution	Purity	Concentration in mother liquor after crystallization
Sucrose	99.99	67.85° Bx
Sucrose + HM (0.05)	99.94	68.00° Bx
Sucrose + HM (0.1)	99.89	68.15° Bx
Sucrose + HM (0.2)	99.79	68.20° Bx

“HM” is high molecular weight impurities, and the figures in the parentheses are the weight of HM added to 100 g sucrose.

Table 4. Effect of HM and invert sugar on hindering effect of crystallization of sucrose

Model sugar solution	Purity	Concentration in mother liquor after crystallization
Raw Sugar B	98.27	68.90° Bx
Sucrose + HM (0.2)	99.79	68.20° Bx
Sucrose + IS (1.73)	98.27	68.20° Bx
Sucrose + IS (1.73) + HM (0.1)	98.17	68.40° Bx

“IS” is invert sugar and “HM” is high molecular weight impurities, and the figures in the parentheses are the weight of the respective substances added to 100 g sucrose.

Table 5. Effect of HM and KCl on hindering of crystallization of sucrose

Model sugar solution	Purity	Concentration in mother liquor after crystallization
Sucrose + HM (0.2)	99.79	68.20° Bx
Sucrose + IS (0.39) + KCl (0.47)	99.13	68.20° Bx
Sucrose + IS (0.39) + KCl (0.47) + HM (0.1)	99.03	68.45° Bx

The figures in the parentheses are the weight of the respective substances added to 100 g sucrose.

Table 6. Viscosity and surface tension of Raw sugar A solution and the UF permeate

Sugar solution	Viscosity (mPa·s) ^{*1}		Surface tension (mN·m ⁻¹)* ²	
	Before UF	Permeate	Before UF	Permeate
Granulated sugar	165	—	77.8	—
Raw sugar A	179	169	69.7	71.6

^{*1} Viscosity was measured at Bx 65° and at 25°C.

^{*2} Surface tension was measured at Bx 65° and at 20°C.

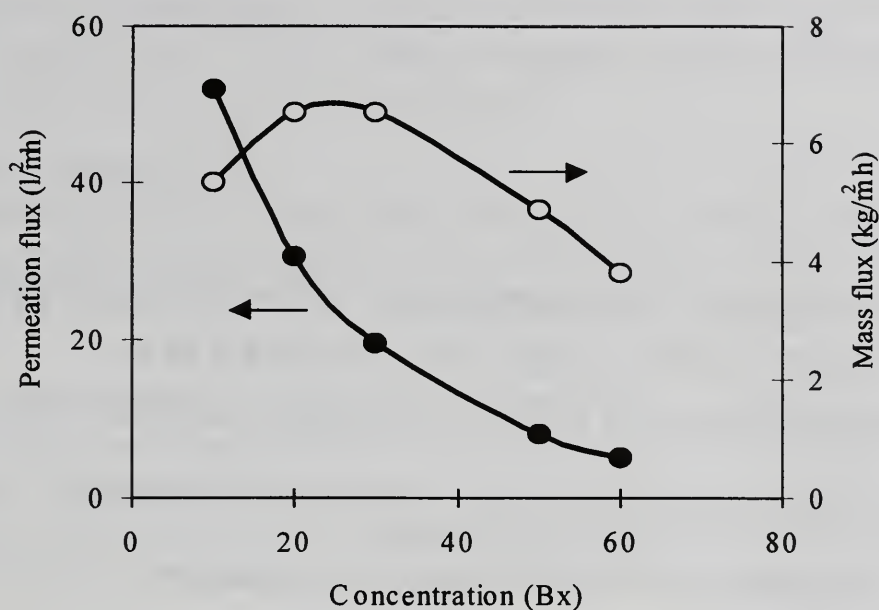


Fig.1. Permeation flux and mass flux in UF of Raw Sugar A solution.

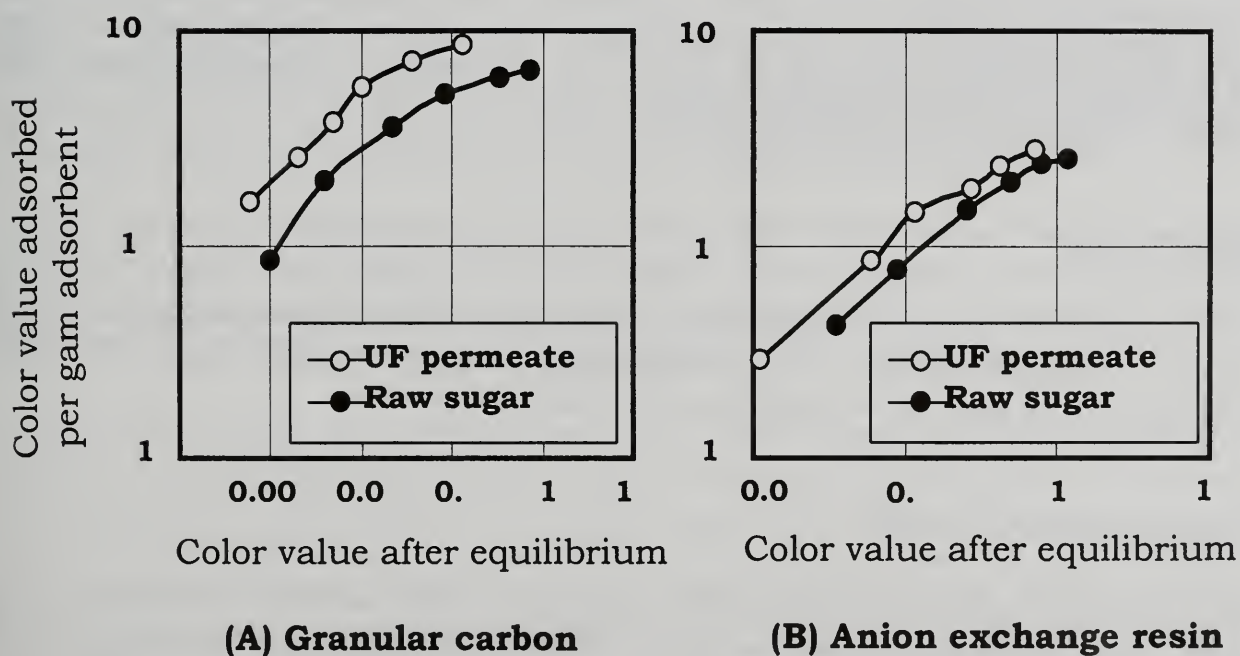


Fig.2. Adsorption isotherm of Raw Sugar A solution and the UF permeate on granular carbon and anion exchange resin

OVERVIEW OF THE DEVELOPMENT AND APPLICATION OF NEAR INFRARED SPECTROSCOPY AT AMERICAN CRYSTAL SUGAR COMPANY

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ABSTRACT

This presentation describes the use of Near Infrared Spectroscopy (NIR) at American Crystal Sugar Company. It describes the use of on-line NIR in our Molasses Desugarization facility to determine sucrose, RDS, betaine, and solution absorbance. Our experience with implementation of AOTF technology is described. The development of calibrations for factory juices with both scanning and AOTF benchtop instruments is discussed. Experiences with transfer of the NIR technology to the factory laboratories are discussed.

INTRODUCTION

NIR has been used at American Crystal Sugar Company over the past several years in both benchtop and on-line applications. Both scanning and acousto-optic tunable filter (AOTF) NIR technologies have been used for both benchtop and on-line applications.

BENCHTOP APPLICATIONS

The objective of the project was to be able to determine a true sucrose measurement in the factory labs. True sucrose data is useful in factory accounting. Prior to implementation of NIR, true sucrose was measured using Ion Chromatograph (IC) at the research center. Use of IC in the factory labs proved to be difficult due to the level of complexity of the instrumentation. There are also time constraints at the factory labs, and the level of expertise of factory lab personnel is a factor.

NIR was chosen for determination of true sucrose measurements in the factory labs because of the ease of operator use and the speed of analysis. Initial calibrations and calibration maintenance were done by research center personnel.

Cossette Sugar Analysis by NIR

The first application that was implemented with NIR was cossette sugar analysis. Cossette extracts were prepared using the standard factory lab procedure of ½ normal weight solutions extracted with aluminum sulfate. Cossette extract samples were analyzed using IC for the NIR calibrations.

The spectrometer used was a NIRSystems (Silver Spring, MD) Model 5000 benchtop spectrometer in the transmission mode. This is a scanning NIR instrument. Initially, a liquid sample module was used with an open top 1mm pathlength quartz cuvette. Problems of cell breakage were experienced due to repeated handling of the quartz cuvette. Frequent cell breakage is undesirable because of cost of cells, and calibrations can change when using a new cell.

A closed cuvette with 1mm pathlength was used. This cuvette could be filled with a syringe while it remained in the cuvette holder. This minimized handling of the cuvette and also minimized cell breakage. The cell was cleaned by rinsing with water. Problems with bacterial growth in the cell were experienced after prolonged use. It was very difficult to remove this bacterial growth due to the small pathlength of the cell.

A liquid sipper module was purchased to replace the original liquid sample module. This module has a peristaltic pump that allows a sample to be pumped into the cell. It also has a cleaning cycle in which the user is prompted to pump a cleaning solution through the cell. This liquid sipper module made the instrument easier to operate for factory personnel.

Both the liquid sample and the liquid sipper module have a heater in the sample compartment to maintain a constant temperature. The 40°C temperature setting was used because it was the lowest temperature that the unit could be set to. Samples had to be pre-heated before being pumped into the cell. The need to pre-heat the samples was a disadvantage.

The calibration equation that was developed for the cossette sugar application was based on 250 samples and was a 6 factor pls equation based on second derivative spectra. The wavelength regions used were 1136-1338 nm, 1510-1836nm, and 2100-2306nm. The regression coefficient was 0.95 and the standard error of prediction was 0.21. The lab error was 0.2. A plot of NIR predicted values versus lab values for cossette sugar analysis by NIR is shown in Figure 1. Figure 2 shows the residual plot for this data.

Cossette Purity Analysis by NIR

At the beginning of the 1999-2000 beet processing campaign, a new method of cossette purity analysis was implemented in the factory labs. For this method, 50% solutions of cossette extracts are prepared, which are extremely turbid and dark. These solutions are analyzed for purity using a polarimeter and refractometer.

NIR was selected to use to obtain true cossette purity analysis in the factory labs. The calibrations were based on IC sucrose measurement and refractometer measurement for RDS.

Because of the goal of having all five American Crystal Sugar Company factory labs capable of running true sucrose measurements, and because of the problems with the NIRSystems unit, a new NIR instrument was selected. Criteria for instrument selection included: ease of operator use, improved sample introduction system, instrument robustness in the factory environment, ease of calibration transfer between five instruments, and ability to analyze both liquid and solid samples on the same instrument.

A Brimrose Corporation (Baltimore, MD) Luminar AOTF-NIR Free Space spectrometer was selected. This instrument was custom designed for American Crystal Sugar Company to accommodate the need for a dual-purpose instrument for both liquid and solid samples, and ease of use for factory personnel. The instrument can be used in the transmission mode for liquid samples and the reflectance mode for solid samples. The instrument is equipped with a 1mm flow-through cell for liquid samples. The cell can be taken apart for cleaning if necessary. Liquid samples are simply poured through a funnel and scanned. The instrument has a rotating sample dish to accommodate solid samples.

The AOTF instrument is solid state and has no moving parts. It is not affected by vibration, which makes the instrument particularly well suited to factory environments. The instrument also has excellent wavelength repeatability which allows for easier calibration between multiple instruments.

The initial calibration equation that was developed for RDS was based on 200 samples and was a 6 factor pls equation. The wavelength region used was 1100-1760nm, the regression coefficient was 0.98, and the standard error of prediction was 0.13. The lab error was 0.10. The initial calibration equation that was developed for sucrose was based on 200 samples and was a 7 factor pls equation. The wavelength region used was 1100-1760nm, the regression coefficient was 0.91, and the standard error of prediction was 0.26. The lab error was 0.20. Plots for these calibrations are shown in Figures 3-6.

These calibrations will be updated for changes in the crop over the campaign, and also for future crops.

ON-LINE APPLICATIONS

The initial on-line NIR application at American Crystal Sugar Company was done at our Molasses Desugarization Plant in East Grand Forks, MN. The instrument used was an early vintage NIRSystems Model SY-4500-P single channel instrument. Sucrose, betaine, RDS, and solution absorbance on the extract, recirculation, and feed molasses streams were measured. Details of this work were presented at the SPRI 1998 conference and also in the International Sugar Journal.

It was decided to upgrade the on-line NIR application to an instrument that could monitor multiple process streams simultaneously. A Brimrose Corporation (Baltimore, MD) Luminar 2060 Lightglide Multiplexer AOTF NIR spectrometer was installed in the Molasses Desugarization Plant. This instrument has a 12 point multiplexer, but it was purchased with only 4 points active. It can be upgraded at a later time to activate all of the channels. The AOTF technology is particularly well suited to process applications because it is not affected by vibrations on the factory floor. Also, the very fast scanning capability is convenient for multiplexed instruments.

The on-line instrument is installed on the extract, recirculation, feed molasses, and raffinate product streams. Calibrations are running for true sucrose, RDS, betaine, and solution absorbance. Data is output in real time to the factory Process Information Management System.

CONCLUSIONS

Benchtop NIR applications have allowed true sucrose measurement in the factory labs at American Crystal Sugar Company. The NIR method has been easier and faster for factory lab personnel to use than chromatographic methods. The on-line NIR applications have made available real time information for process decision making.

The calibrations that have been developed for the NIR applications will continue to be upgraded to include changes in the beet crop during storage, and also to include future crop years. This will result in making the calibrations more robust.

The development of the NIR applications will continue at American Crystal Sugar Company. Potential applications for NIR technology are abundant throughout the factory.

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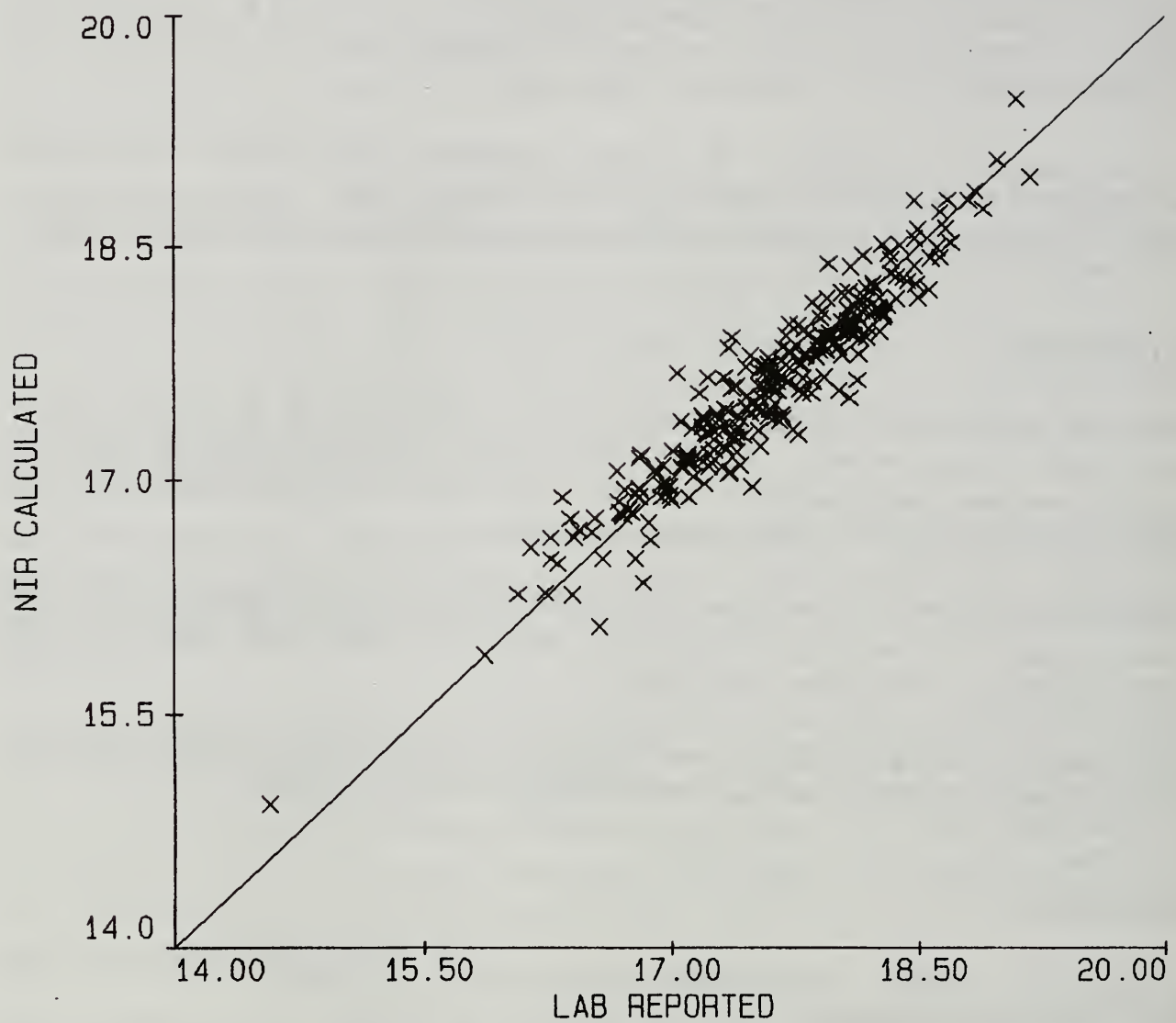


Figure 1. Cossette Sugar: NIR predicted vs. Lab

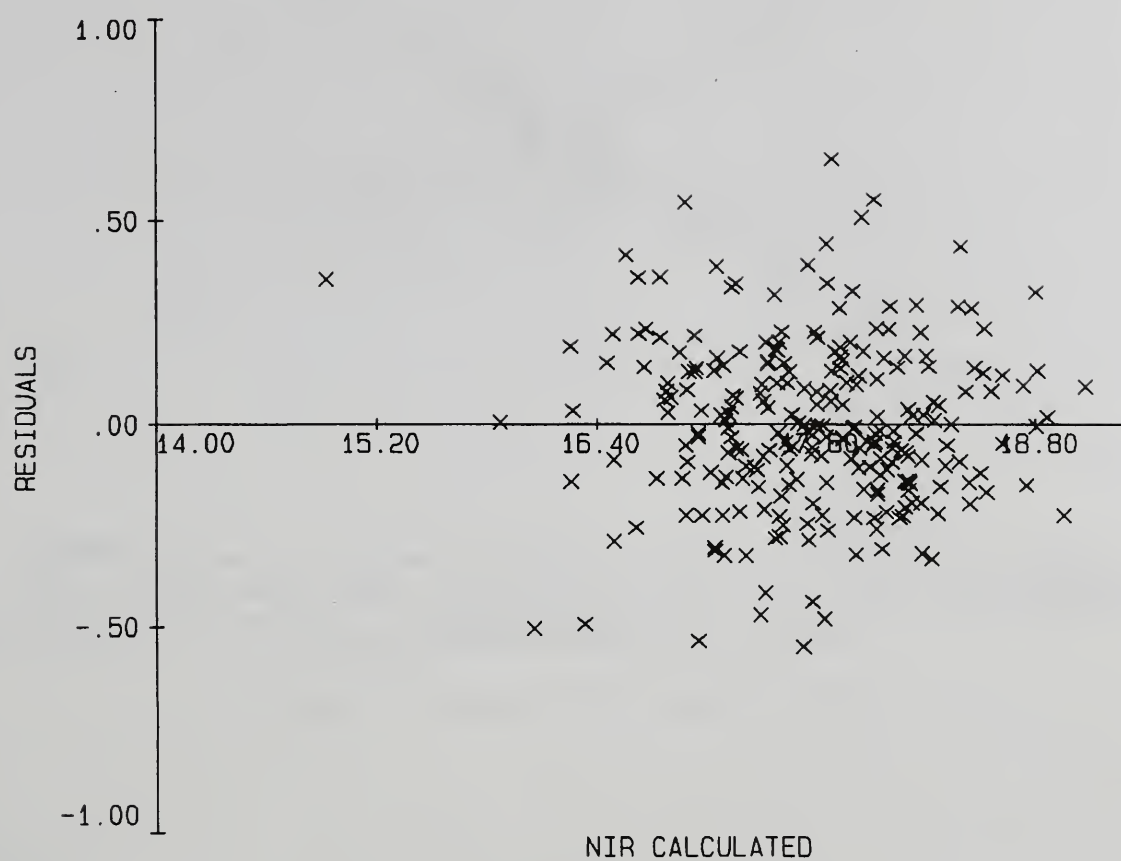


Figure 2. Cossette Sugar: Residual Plot

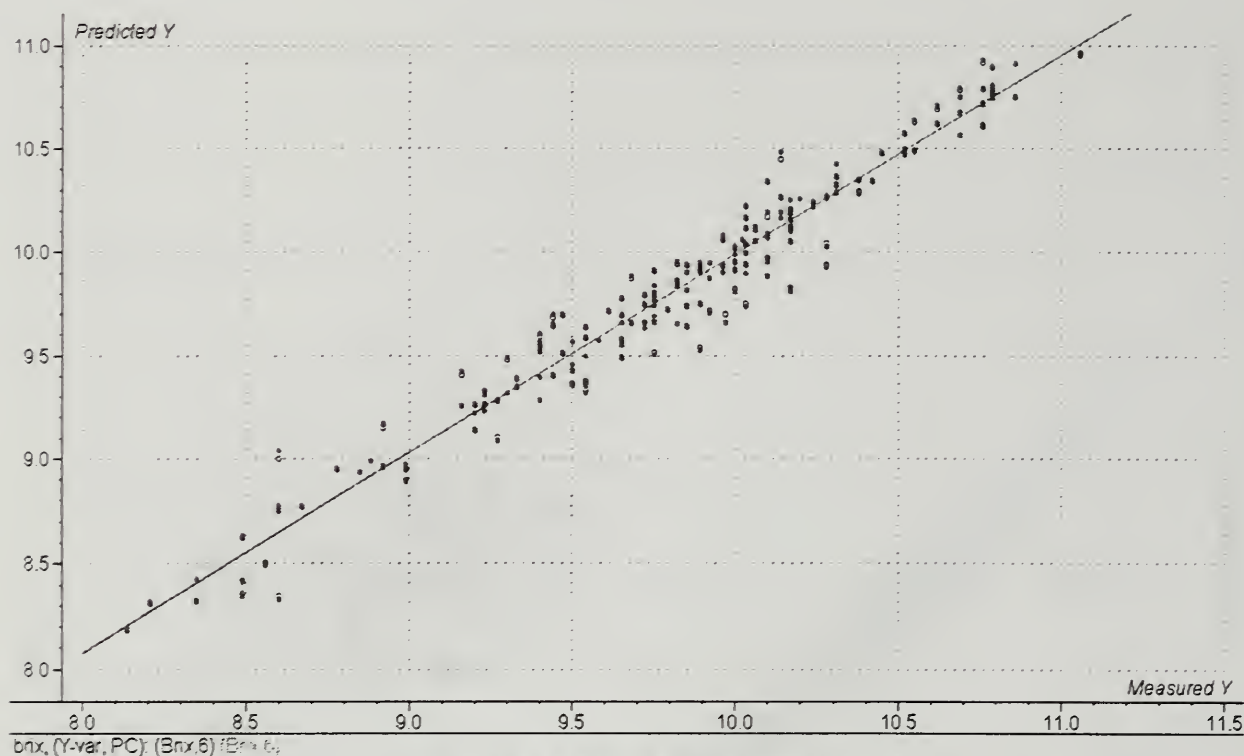


Figure 3. RDS: NIR predicted vs. Lab

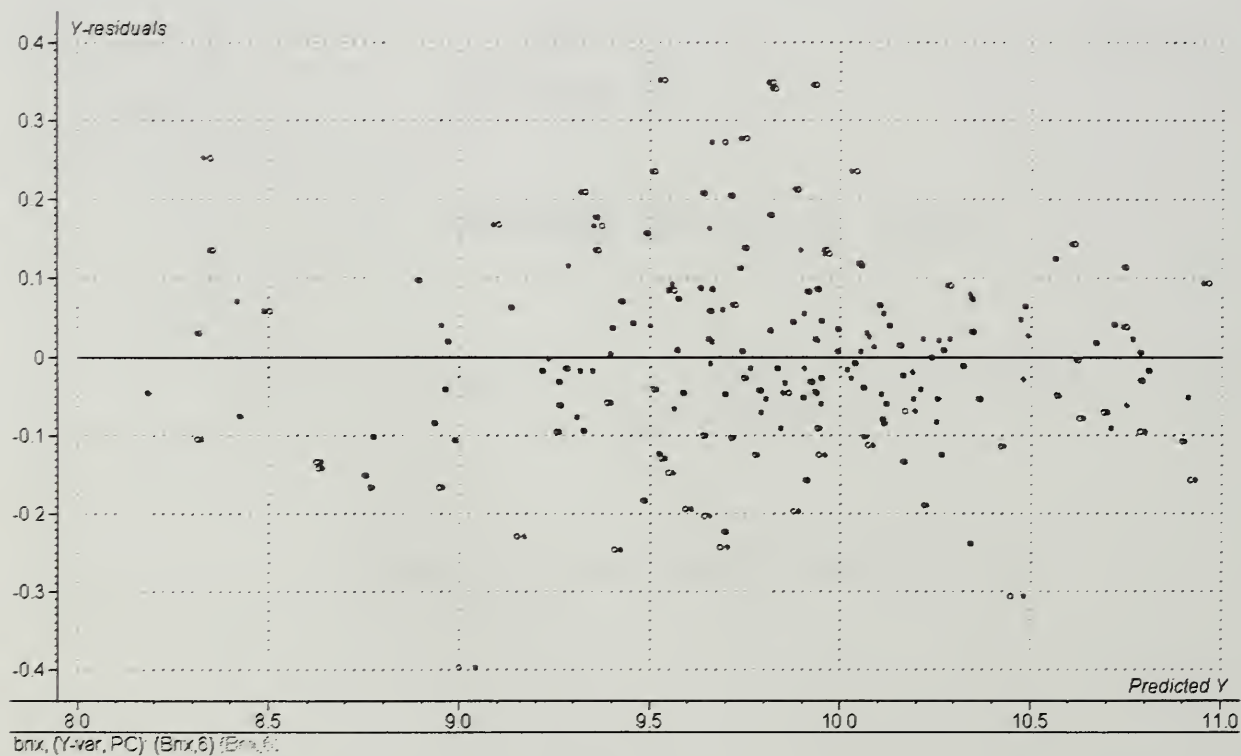


Figure 4. RDS: Residual Plot

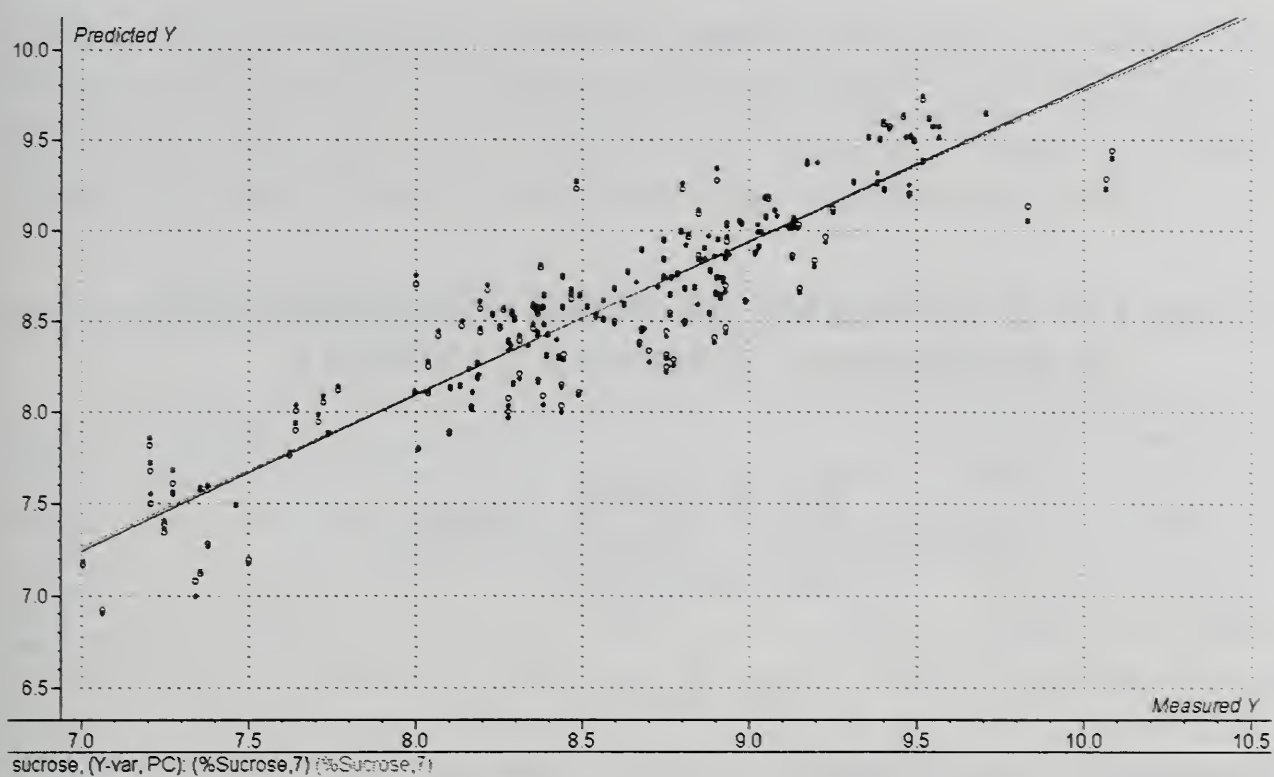


Figure 5. Sucrose: NIR predicted vs. Lab

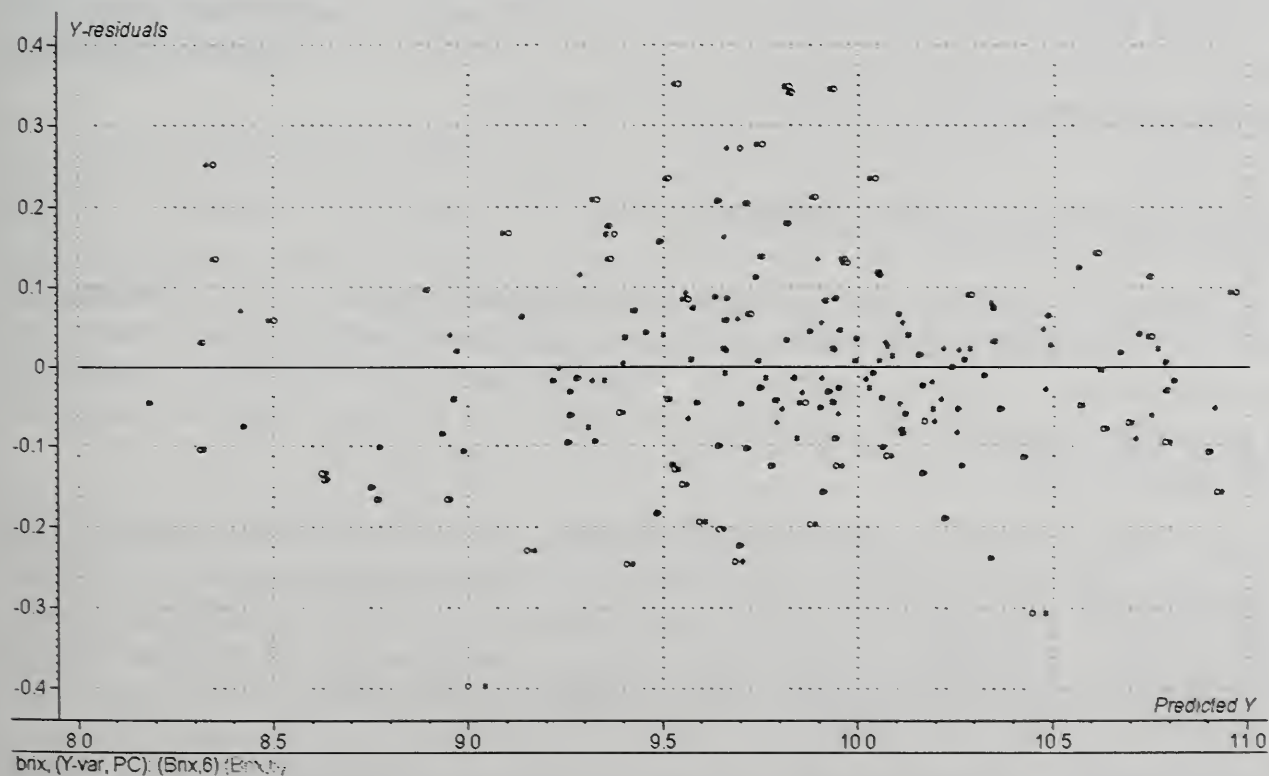


Figure 6. Sucrose: Residual Plot

CANE JUICE ANALYSIS BY NEAR INFRARED (NIR) TO DETERMINE GROWER PAYMENT

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ABSTRACT

As applications of NIR analysis are increasing in the grain and food industries, more options are becoming available for analysis of incoming sugar cane in the factories. For the 1999-2000 crop season, Sugar Cane Growers Cooperative of Florida (SCGC), together with Florida Crystals Corporation, has adopted Near Infrared (NIR) spectroscopy as the standard method for cane juice analysis. This paper will include a brief history of cane juice analysis at SCGC as it has evolved from polarization using lead clarification to polarization using NIR spectroscopy. Experiences with data acquisition, equation development, and equation validation, necessary for implementing NIR analysis, will also be discussed.

THE GOALS OF CANE JUICE SAMPLING

The process of analyzing incoming sugar cane for grower payment can be a challenge to many factories. A uniform method is difficult to standardize throughout the industry since many variables exist between one factory and another. Variables such as the size and the number of growers should be considered when developing the process for analyzing either the sample of cane or the sample of juice.

Sugar Cane Growers Cooperative of Florida grinds close to 22,000 tons of cane per day on average and brings over 1,000 loads of cane daily from over fifty grower members. With the goal being to collect a sample from every 65 tons of cane, this presents a sampling challenge. Assuming that each trailer carries approximately 20 tons of cane, a sample will be collected from every third trailer for each grower for each field harvested on any given day.

This sampling has been fine-tuned over the last two years to optimize efficiency. Where in earlier years, 600 samples were collected in 16 hours for 19,000 tons of cane, now 350 samples can be collected in 10 hours for 22,000 tons of cane. This may not seem to be a significant improvement, but before, although there were upwards of 600 samples, there were

occasions during the crop where insufficient samples were obtained for a particular grower. Now, on the other hand, the 350 samples are sufficient to complete the grower sampling. Trucks are dumped at a rate of up to 28 trucks per hour on each milling tandem. The sampling method must be able to analyze at a rate of one sample every two minutes. Where older methods could not analyze the cane juice samples at this rate, the NIR instrument can do it easily.

EVOLUTION OF METHODS OF CANE JUICE ANALYSIS

The procedures for sampling and analysis of incoming cane have changed over the years. The earlier method of juice analysis used the brix hydrometer for determining the juice density. The percent sucrose was determined by polariscope reading converted to sucrose using the Schmitz Table with lead subacetate (and later Horne's dry subacetate of lead) for juice clarification. The use of lead salts for clarification lasted until the late 1980's, when government regulations for disposal of heavy metals became more stringent. Formidable research¹⁻⁵ had been performed during the 1970's and 1980's for a replacement clarification method using aluminum salts. In 1988, SCGC replaced the dry lead salt with the aluminum salt, aluminum chloride, in combination with calcium hydroxide, and used this mixture to clarify cane juice samples in the laboratory. The computer programs converted the pol results from the aluminum chloride/calcium hydroxide clarified juice to the standard lead method equivalent pol, using a regression analysis equation. About the same time, paired comparison tests were performed at the U.S.D.A. – A.R.S. in Houma and at SPRI in New Orleans³ between lead subacetate and the aluminum chloride/calcium hydroxide combination. The results of the aluminum chloride/calcium hydroxide polys proved to have superior correlation with the lead method equivalent polys.

For two years, incoming cane juice was analyzed using the aluminum chloride/calcium hydroxide clarification for pol determination, and hydrometer spindle for brix determination and, although this method was reliable, it was time consuming. During this time, the total tons of sugarcane harvested at SCGC grew by almost 20%, resulting in an increase in juice samples/hour for analysis in the laboratory. At these higher sampling rates, it was nearly impossible for the chemists to keep up with the sampling requirements. A method of analysis had to be found that could analyze samples at a higher rate of speed.

In 1990, the methodology changed again as the solution for faster analysis was mechanical clarification rather than chemical clarification. This mechanical clarification was found in the form of the Membrex ultrafiltration membrane. To help increase the speed of analysis, brix determination by spindle was changed to refractometric analysis. A flow through system was devised whereby the cane juice sample that was pumped into the laboratory flowed directly from the membrane filter to a refractometer and to a polarimeter. The entire analysis took less than three minutes. The cane juice emerged from the 0.01 micron pore size membrane a brilliant golden color, and could easily be read by the refractometer and the polarimeter. These advances in analytical techniques were advances only in the laboratory. The data that emerged from the laboratory for grower payment was correlated back to the nearly obsolete lead pol and spindle brix that the growers were accustomed to seeing. Once again, regression analysis equations were updated in the computer programs to correlate the Membrex clarified juice pol

and the refractometric brix. Although the Membrex system brought with it a myriad of problems, it became the method of choice for the Florida mills for almost a decade.

INITIAL PROPOSAL

Throughout the 1990's, SCGC investigated and tested alternative methods of cane juice analysis. During the 1998-1999 season, a collaborative effort was made between the three mills of Florida Crystals Corporation, and Sugar Cane Growers Cooperative, to develop a uniform equation where the same sample of cane juice would produce the same analytical results in the four laboratories. The NIR instrument that was selected for measuring cane juice in all four laboratories is the Routine Sugar Analyzer with beverage module and 5000 monochromator with wavelength range of 1100-2500 nanometers. In the cane juice spectrum, (see Figure 1), the wavelength range used for analysis is 1250-1820 nm, and 2120-2330 nm.

MODEL DEVELOPMENT AND POPULATION STRUCTURING

Beginning in 1998, almost 900 samples were collected, scanned and analyzed by the four laboratories throughout the season. A flowchart for calibration and implementation of NIR analysis is shown in Figure 2. Once the cane juice samples have been collected, near infrared spectral data must be obtained, along with accurate reference method analysis for each sample. The reference method used for cane juice NIR correlation is pol clarified with ABC Sugar Clarifier ®, and spindle brix. The spectral data and the reference data are used as the basis for population structuring.

The key to population structuring is the collection of representative samples. Samples that exemplify the varying characteristics anticipated during the span of the season such as maturity, soil type, quality of cane, and quantity of mud, and if available, pre-harvest (immature) cane juice samples and freeze damaged cane juice will help make the equation more robust. The purpose of population structuring is to identify the "best" samples by removing redundant samples and spectral outliers. Using Chemometrics, the software combines the spectral data and the reference data, performs a regression analysis and generates a model to predict the constituents of interest, in this case, pol and brix. The software uses second derivative math for the enhancement of the near infrared spectra, and modified partial least squares (MPLS) regression for the development of the calibration equation. The results of the preliminary equations for brix and pol are shown in Figure 3. After the equation has been developed, its performance is measured by using it in parallel with the wet chemical analysis to determine if the equation is satisfactory. If it is acceptable, it is implemented into the routine operations.

MODEL VALIDATION AND UPDATING

The NIR analysis performed on each sample is a prediction of the juice sample based on calibration data stored in the software, and as with most natural products, sugarcane juice will change throughout the season, due to soil composition, rainfall, and other growing conditions.

Because of this, it is necessary to periodically validate the equation against the reference method. Validation will measure the prediction accuracy of the NIR calibration. It is done by acquiring spectra and performing wet chemical analysis on a separate set of samples, similar to those used for the mathematical model, but that have not been used to develop the model. Validations at SCGC are performed weekly. Figure 4 shows examples of early and recent validation results. If the validation results are acceptable, they can be included in the model. Updating the model with accurate validation data will make the equation more robust, (see Figure 5 where the improvement in the current equation over the preliminary equation is evident).

As routine analyses are performed, the instrument may detect a sample that it does not recognize as being similar to other samples. The software will flag this sample as an outlier. Outliers can be caused by conditions such as ambient vibrations, a change in ambient temperature, a contaminated sample, a sample with an unusual temperature, or a sample from an unusually muddy field. Samples that are identified by the equation as neighborhood outliers should be analyzed by the reference method, and if they are genuine, uncorrupted samples, should be added to the calibration data to update the equation. Updating the equation with special event data will make the equation more robust.

During the 1999-2000 season, the initial plan for updating the model included collecting 50 samples each week to add to the calibration equation in order to capture the subtle changes that occur in the cane juice throughout the crop. However, there were occasions where a more aggressive sampling schedule was necessary. During these situations, 250 samples were added to the equation for the week. This occurred at the beginning and near the end of the season, when the cane juice composition was different than it had been when the equation was first developed. Immature cane, early in the season, and exceptionally muddy cane, late in the season were two of the reasons for the change in juice composition. Signs that may indicate that updating is needed include unusual NIR results, poor correlation between instruments, and an excessive number of neighborhood outliers. With the NIR, in contrast with the polarimeter and the refractometer, the chemist's ability to tune in to the instrument's sensitivity is essential.

INSTRUMENT DIAGNOSTICS

The NIR software is able to perform self-diagnostic tests as per the user's request. Diagnostics is composed of three separate tests: instrument response, wavelength accuracy, and repeatability. Instrument response tests the performance of the detectors. Wavelength accuracy checks the wavelength alignment of the instrument. Repeatability checks the optical data at each wavelength. It is important to not only perform the diagnostics, but to look for any trends that may occur in the diagnostic data. This can serve as a quality control tool. For analysis of grower samples, the chemists at SCGC perform the instrument diagnostics daily on each instrument. The results can be printed daily, or as often needed.

SUMMARY AND CONCLUSIONS

The overall performance of the NIR during the 1999/2000 crop season has been satisfactory. The NIR requires little to no maintenance, other than an annual lamp replacement. There are no harsh chemicals used for clarification or cleaning. There is no need for sample preparation. The instrument is simple to operate for routine analysis, though the data manipulation can be challenging. There is ample support from the manufacturer while designing and implementing the calibration process. In addition, a four-day training session is included with the purchase of each instrument. Analysis on growers' samples can be performed in less than one minute. Precise correlation can be obtained and maintained with appropriate quality control measures, such as diagnostic testing, equation validation and equation updating. This requires a dedicated chemist available to perform the wet chemical analysis and data manipulation on an as-needed basis. Other than the initial purchase of each instrument and the sample cups, no other expenditures have been made for the instrument to analyze incoming cane juice during this first season of operation. In contrast, the method used for ten years prior to the NIR, the Membrex membrane, polarimeter and refractometer, resulted in repairs, replacement parts, and replacement membranes totaling approximately 15,000 USD per year.

For the 2000-2001 season, development of NIR applications for the process laboratory will continue at SCGC along with plans to determine potential on-line applications in the factory.

ACKNOWLEDGEMENTS AND DEDICATION

The success of this project is the result of the efforts of many people. The author would like to acknowledge the contributions made by the chemists who were vital to the development and implementation of NIR spectroscopy at SCGC: Marcus Giddens, Aubrey Trotman, Candy Alfonso, Donald Boudreaux and Michael Carkey.

This paper is dedicated to the late Margaret A. Clarke, an extraordinary woman, friend, and scientist, and the impetus behind NIR spectroscopy in the sugar industry.

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Figure 1

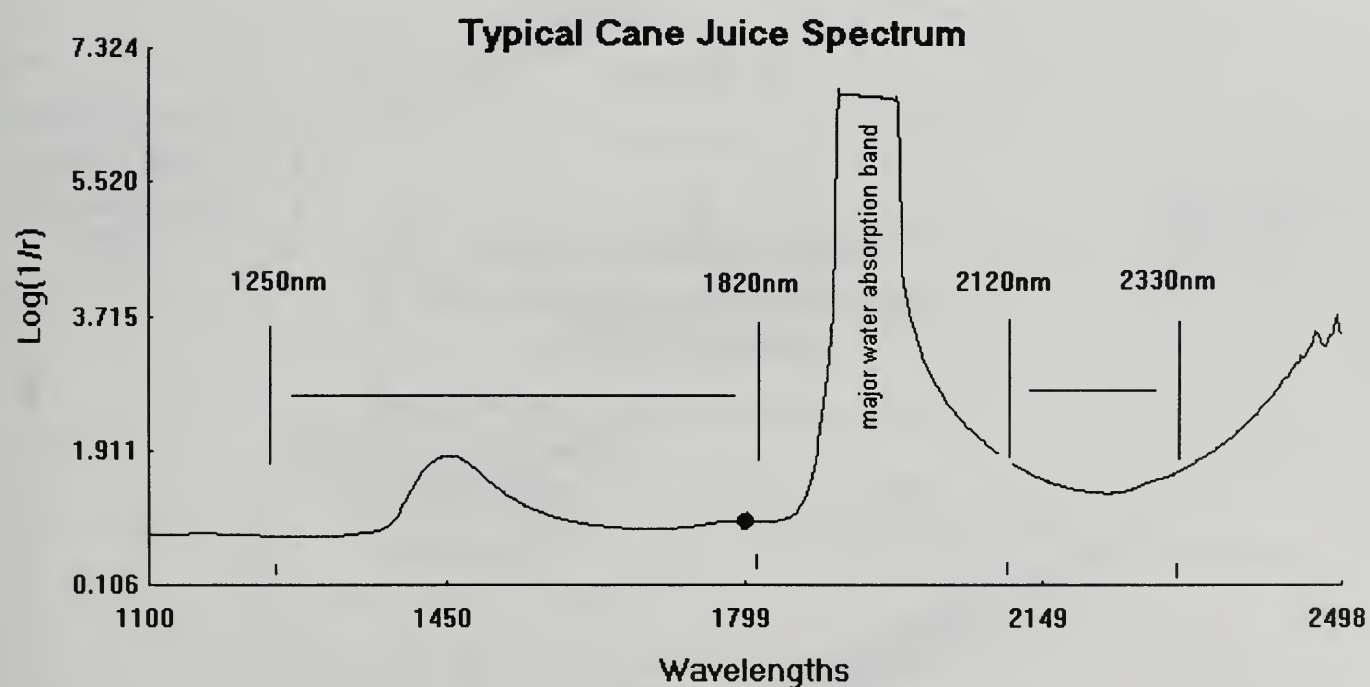


Figure 2

SCGC Calibration Flowchart for NIR

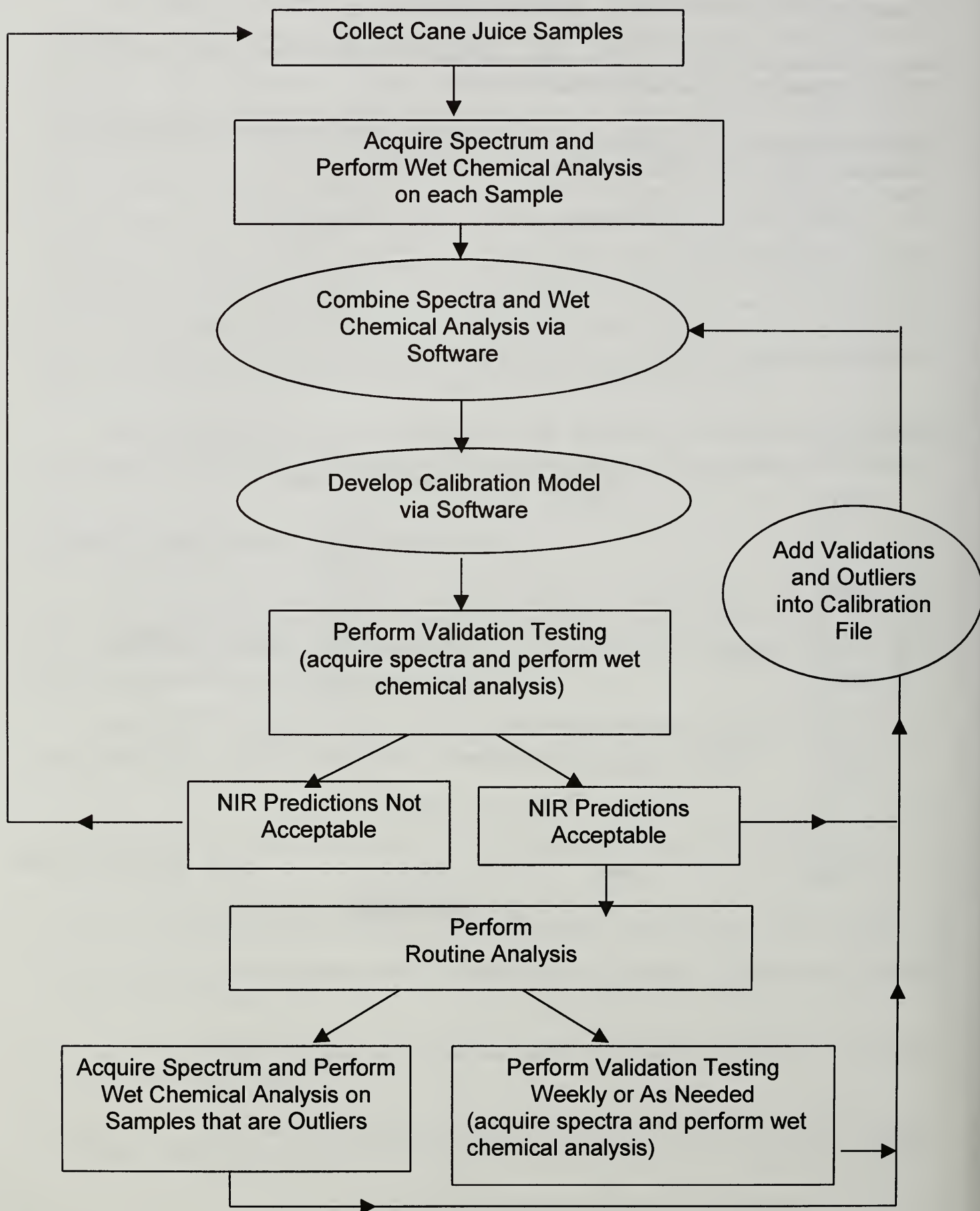


Figure 3 Preliminary Equations

Constituent	RSQ	SEC	Samples
Brix	.966	.246	886
Pol	.958	.182	886

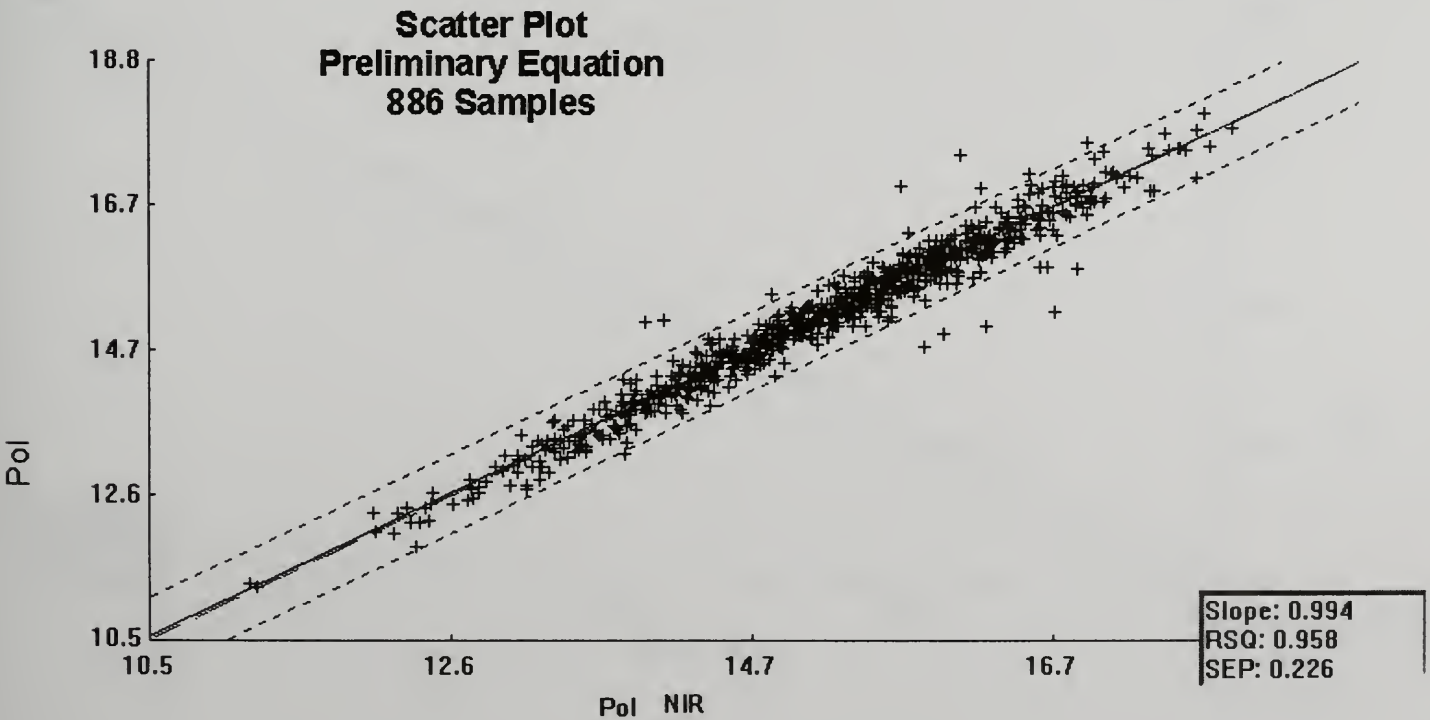
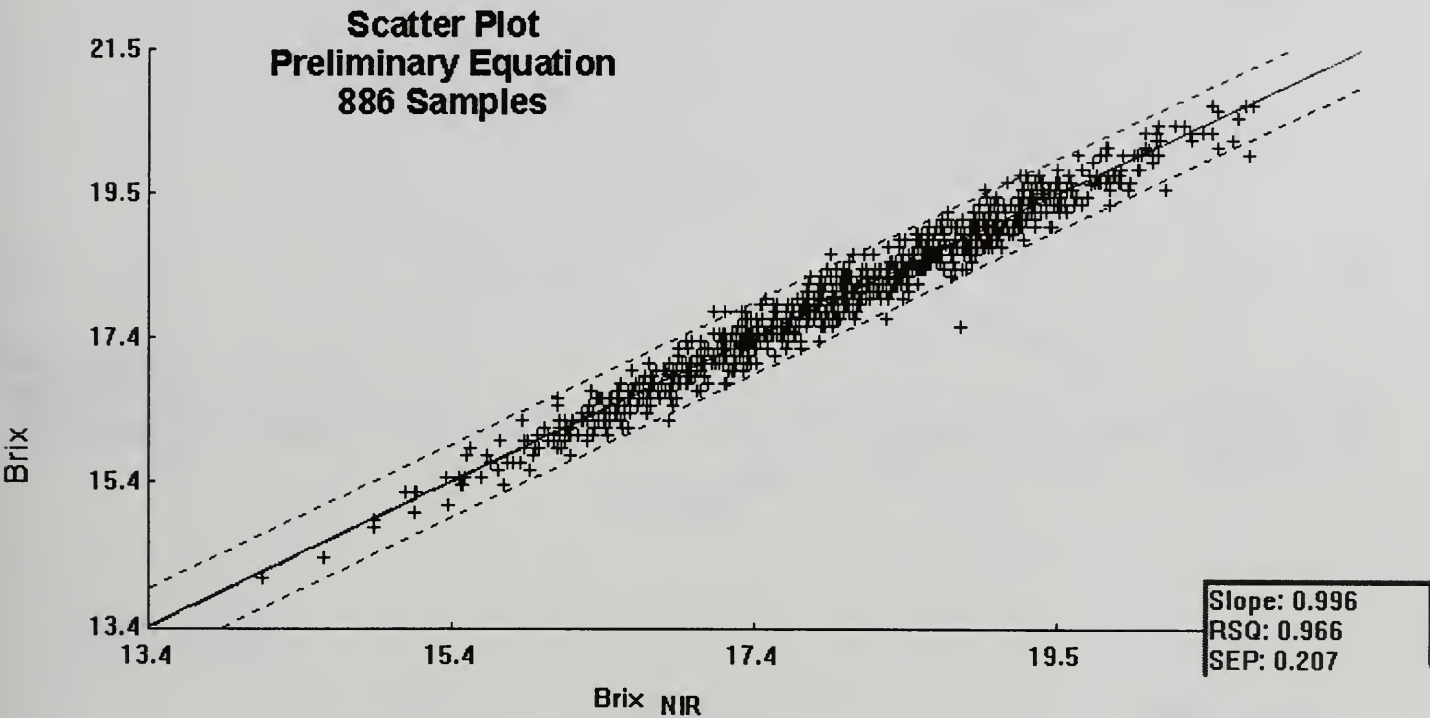


Figure 4

Early Results of Validations

RSQ: 0.955

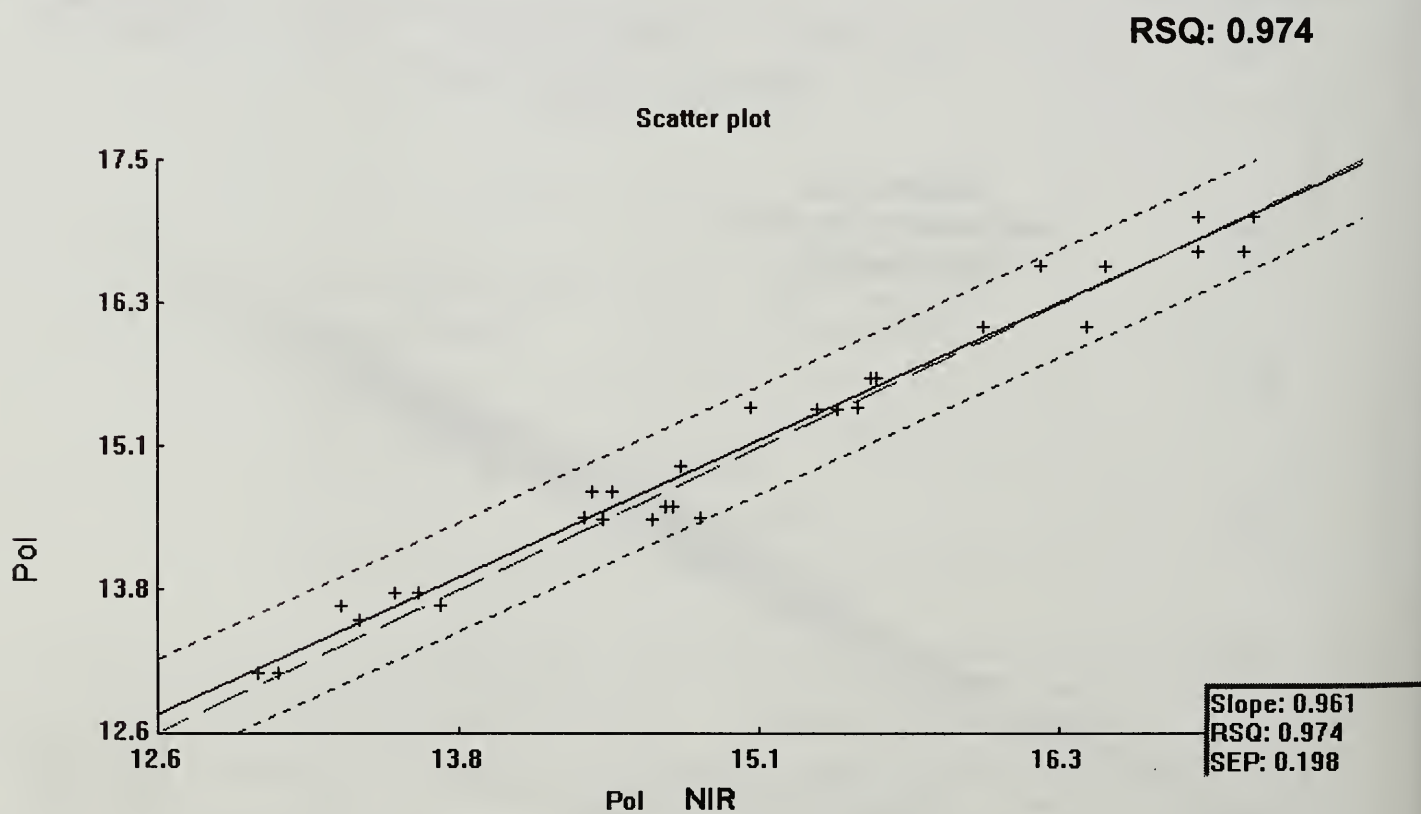
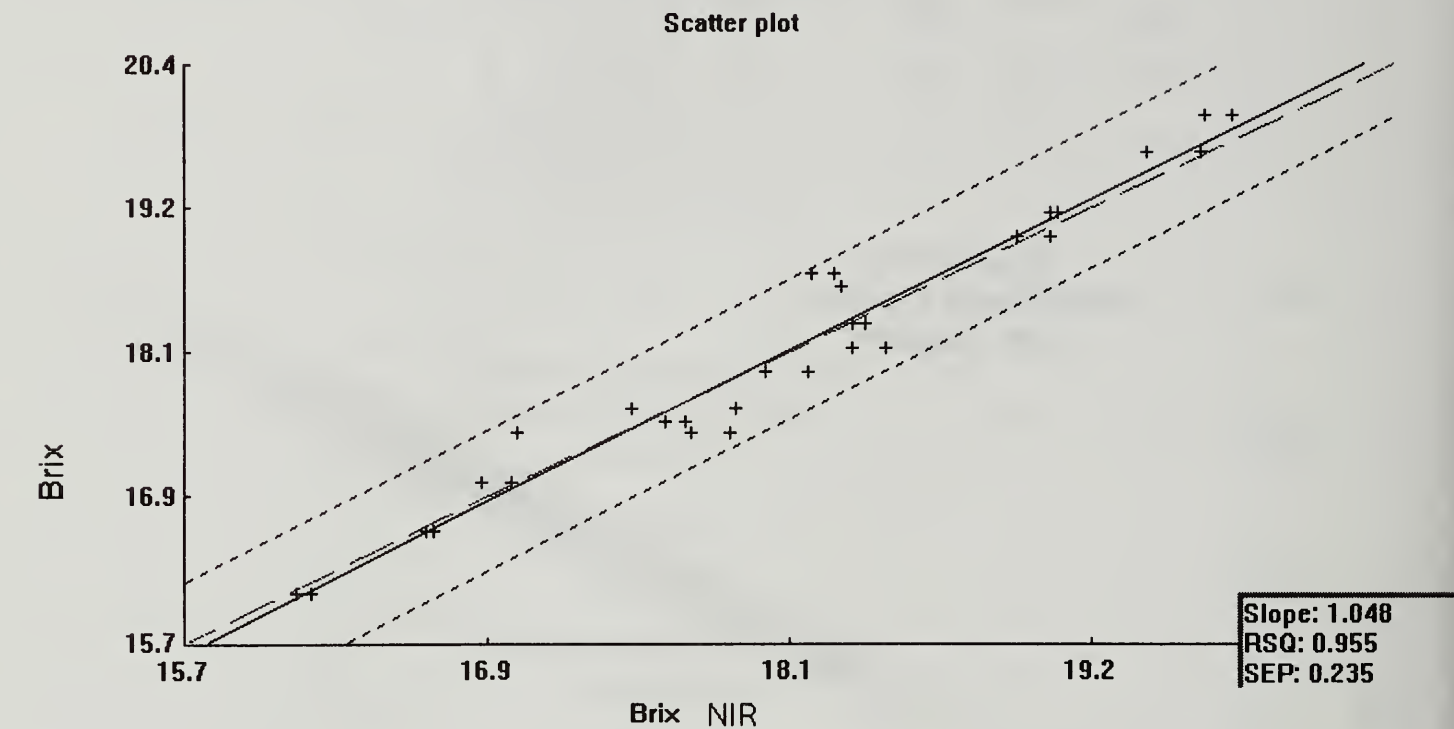
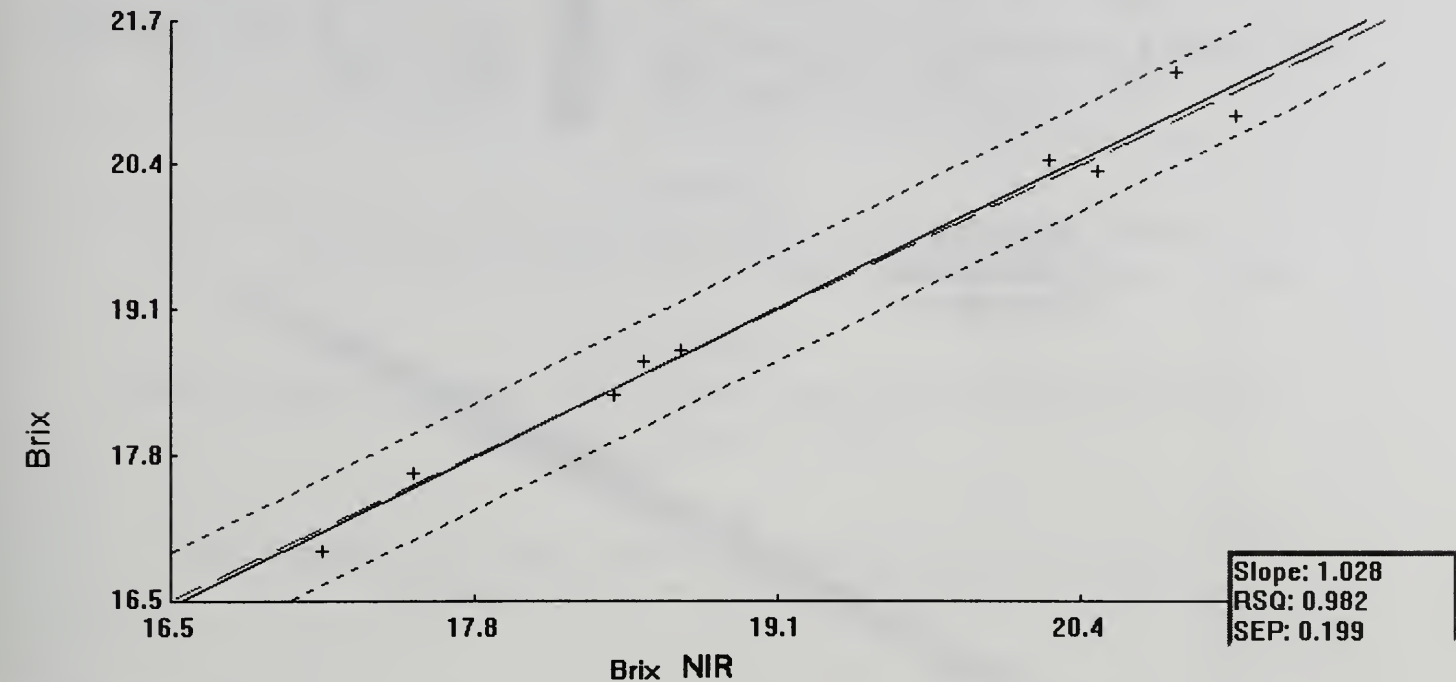


Figure 4 (cont.)

Recent Results of Validations

RSQ: 0.982

Scatter plot



RSQ: 0.987

Scatter plot

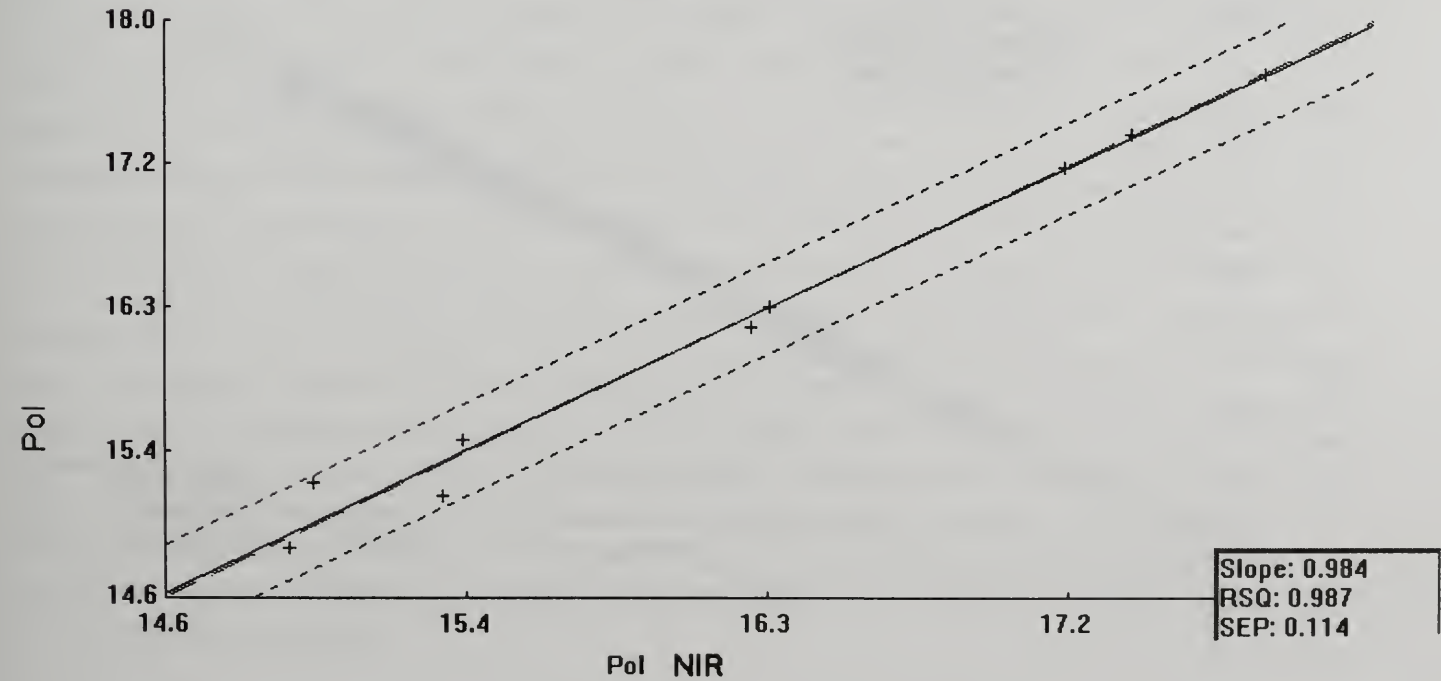
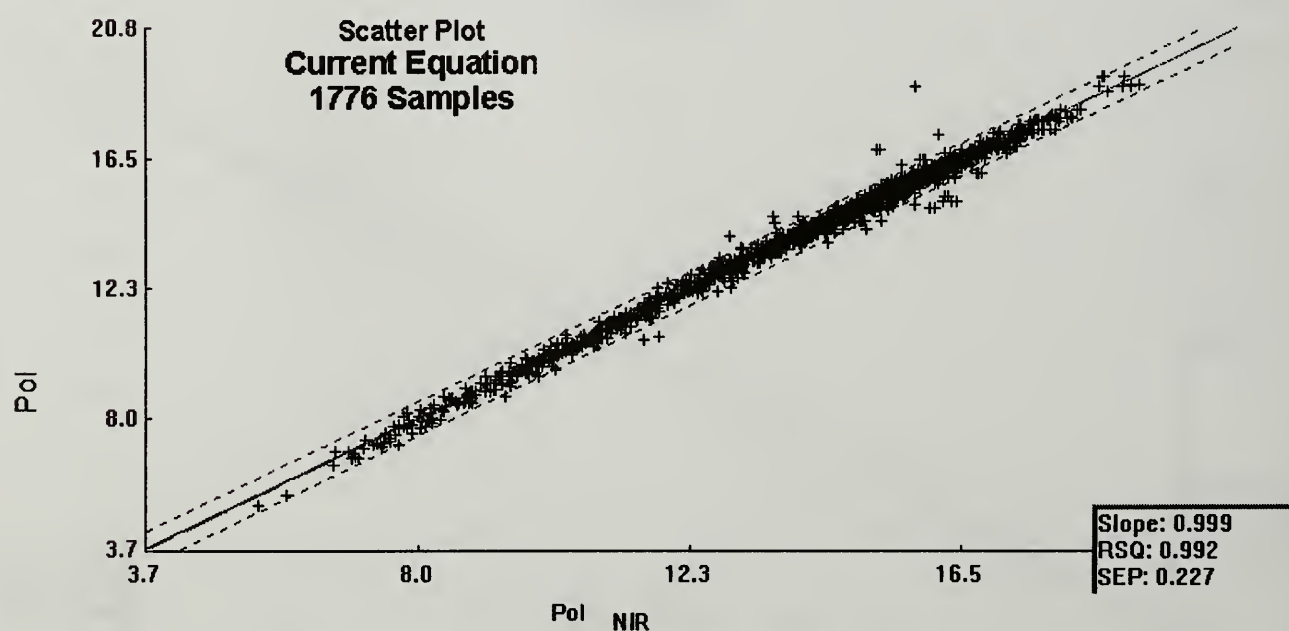
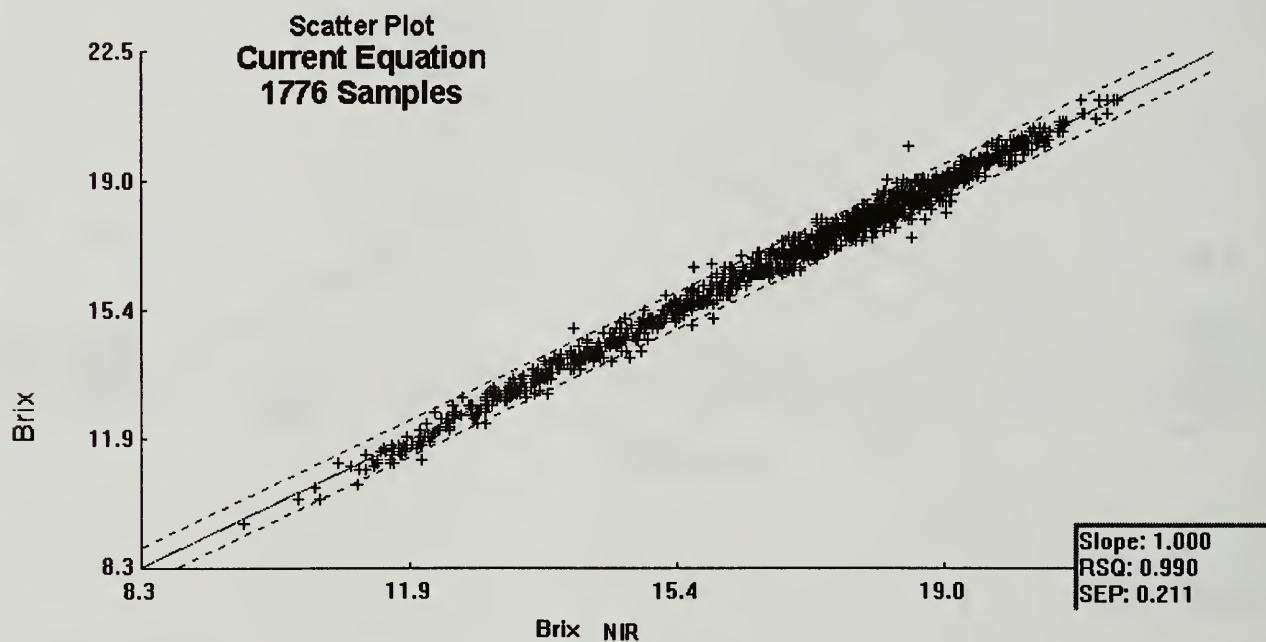


Figure 5.

Preliminary Equation**Current Equation**

Constituent	RSQ	SEC	Samples		RSQ	SEC	Samples
Brix	.966	.246	886		.990	.196	1776
Pol	.958	.182	886		.992	.181	1776



EFFECT OF HARVEST METHOD AND STORAGE TIME ON SUGARCANE DETERIORATION

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ABSTRACT

The recent increase of billeted cane being mechanically harvested in Louisiana has often meant an increase in deteriorated cane being processed. Some of this deterioration in cane quality, i.e., the increase in associated trash (i.e. leaves, tops and field soil) is not necessarily a function of the newer harvest method, per se, but rather a function of mechanical harvesting in general. Further, there is the occurrence of sugar destruction in the cut cane between harvesting and crushing, regardless of the harvest system. There is a real need to establish new criteria for levels of deterioration in Louisiana cut cane, in order to better predict: 1) the quality of the cane to be processed and, 2) the effect of harvest methods and storage conditions. In this study, there were eight cane supply treatments, with samples taken on each day for four consecutive days (0, 24, 48 and 72h) before laboratory milling. Treatments included handcut (control) net, green and burnt standing whole-stalks taken from field plots each day. Soldier harvested burnt, green, and stored burnt whole-stalks were chosen to simulate cane from a heap or transloader stack each day. Burnt and green billeted cane were also taken to simulate cane from a billet wagon each day. Initial color for all cane treatments was associated with leaves and tops; color formed dramatically in the burnt billeted cane with storage time. Glucose and fructose were consistently greater in billeted than whole-stalk cane. Dextran and oligosaccharide formation was also greater and more rapid in billeted cane than whole-stalk cane, and concomitant with a decrease in pH. Billeted cane deterioration occurred earlier than in whole stalk cane, with burnt billeted cane deterioration more rapid and extensive than in green billeted cane. Oligosaccharide formation in cane is discussed in detail, with emphasis on both kestoses (up to GF₅) and dextran oligosaccharides. Optimum postharvest handling conditions to minimize grower and factory losses are discussed.

INTRODUCTION

Whilst the mechanical harvesting of billeted sugar cane has increased sugar yields /acre, an increase has also often been experienced in the impurities brought to the factory. Such impurities not only occur because of associated trash (i.e. such as leaves, tops and field soil), but also because of sugar destruction in the cut cane between harvesting and crushing. Sugar destruction reactions include chemical and enzymic reactions in the cane, and those from microorganism activity, and can also be influenced by cane health and environmental conditions. There is, therefore, a real need to establish new criteria for levels of deterioration in Louisiana cut cane, in order to better predict the quality of the cane to be processed and the effect on process conditions and raw sugar quality.

Sugar technologists (see Smythe, 1967; Montavani et al, 1986; Morel du Boil, 1991, 1992, 1995) have reported a variety of cane deterioration products that can be used to confirm cane delay and, consequently predict and control processing problems at the factory. Such deterioration products have included high invert concentrations, yeast contamination (e.g., alcohol concentrations) and polysaccharides, but not all deterioration products impact future factory processes. Dextran polysaccharide has often been reported as a deterioration product that does impact (negatively) factory processing because, as a gelling polysaccharide, it causes viscosity increases in process streams. However, many sugar technologists (see Morel du Boil, 1995) now believe that while dextran and other polysaccharides increase process stream viscosities and slow down crystal formation they do not have a noteworthy effect on sugar crystal elongation. This crystal deforming effect has been ascribed rather to oligosaccharides, and some technologists (Ravelo et al, 1991b) believe that oligosaccharides reflect more widely future factory processing problems. Morel du Boil (1995) observed that oligosaccharides, particularly kestoses, increased in deteriorated cane, and Ravelo et al (1991b) reported that the formation of total oligosaccharides was greater than the formation of dextran in cane subjected to delays and is, therefore, a more sensitive indicator of cane deterioration.

This proposed study was undertaken to determine the effect of various harvest methods and storage times (to simulate cut-to-crush cane delays) on cane deterioration. A major goal of the study was to identify compounds which can be used as criteria to assess the extent of deterioration of cane after cutting. Because of the lack of information on what specific oligosaccharides form on cane deterioration and delays, and the direct impact oligosaccharides have on processing, some emphasis was placed on oligosaccharide formation. A secondary goal was to determine optimum postharvest handling conditions to minimize grower and factory losses.

EXPERIMENTAL

Sample Preparation

The cane variety in this study was LCP 85-384. Each cane sample (whole-stalk samples consisted of 15 stalks or approximately 30 lb; billeted cane samples were based on weight of 15 - 25 lb) was weighed to determine mean stalk weight. Samples (whole-stalk samples were first cut into billets approximately 12-18 in long using a commercial-type saw) were passed through a prebreaker similar

to the one used by most commercial mills in Louisiana to prepare the sample for analysis according to the procedure described by Legendre (1992). A 1000 g sample of the prepared cane was pressed for 1 min 15 secs at 3,000 psi. The press separated the sample into juice (60 - 80% extraction) and residue (bagasse).

Cane Treatments

There were the eight treatments (denoted A to H) which are listed in Table 1. The eight treatments were milled each day for four days (0 to 72h) with eight replications per treatment; stored treatments were weighed at cutting, reweighed each day and weighed prior to milling. Handcut A, B and C (control) treatments and machine cut field storage treatments D and E, were obtained directly from the field, and outside ambient temperatures were : 45-77F (0h); 58-81F (24h); 58-74F (48h); and 42-46F (72h). Machine cut F - H treatments were placed in a greenhouse which was set up to simulate typical outside humidity and temperature conditions during storage in delivery wagons. Humidity in the greenhouse generally ranged from 60% (days) to 100% (nights) for each date. The temperature of the greenhouse for the duration of the study was as follows: 75-90F (0h); 75-90F (24h); 70-90F (48h); and 65-75F (72h).

Theoretical Recoverable Sugar (TRS)

The pressed cane juice was analyzed for Brix (by refractometer) and pol (by polarimeter using the method stated in Chen and Chou (1993)). The bagasse residue was analyzed for moisture (by drying for 24-48h at 150 °F). The Brix, sucrose (pol), and fiber percent cane and yield of theoretical recoverable sugar (TRS) per ton of cane were calculated from these analyses (Legendre and Henderson, 1972).

Dextran

Replicate samples were analyzed for dextran using two methods. The Rapid Haze method of Clarke et al (1987) and the ASI (Audubon Sugar Institute) II method by Sarker and Day (1986) which utilizes dextranase enzymes.

For the following quality parameters, composite samples (10g each of eight replicates combined) were analyzed:

Brix

The mean Brix of triplicate samples was measured using a Leica Abbe Mark II Refractometer with a crosshair reticule.

pH

pH was measured at room temperature (~25 °C), using an Ingold TM combination pH electrode calibrated at room temperature using two different pH buffers (pH 7 and 10). The electrode was connected to a Metrohm 716 DMS pH meter.

Color and Turbidity

Color and turbidity were measured as the absorbance at 420nm and calculated according to the official ICUMSA method GS2/3-9 (1994). Samples were diluted in triethanolamine /hydrochloric acid buffer (pH 7) and filtered through a 0.45 µm filter.

Table 1. Cane harvest treatments.

Treatment	Description of Treatment
HAND CUT	
A - NET CANE, WHOLE-STALK	Unburned field plot, stripped of all leaves. 1 set of samples (8 replications)/24h.
B - GREEN STANDING, WHOLE-STALK	Unburned field plot, without stripping. 1 set of samples (8 replications)/24h.
C - BURN STANDING, WHOLE-STALK	Burned field plot, without stripping. 1 set of samples (8 replications)/24h.
MACHINE CUT	
D - GREEN HEAP, WHOLE-STALK	Soldier harvested 0h, placed on heap, samples taken each day without stripping or burning. 1 set of samples (8 replications)/24h.
E - BURN HEAP, WHOLE-STALK	Soldier harvested 0h, placed on heap, samples taken each day without stripping. 1 set of samples (8 replications)/24h.
F - N DAY OLD STORED BURN WHOLE-STALK	Soldier harvested 0h, no stripping, stored in transloader stack conditions for 24, 48 and 72h before milling.
G - N DAY OLD STORED GREEN BILLET	Cane cut with combine; no stripping, billeted and stored in billet wagon conditions for 0, 24, 48 and 72h.
H - N DAY OLD STORED BURN BILLET	Cane cut with combine; no stripping, billeted and stored in billet wagon conditions for 0, 24, 48 and 72h before milling.

Chemicals and Reagents

HPLC grade sodium hydroxide and sodium acetate trihydrate were obtained from Fisher Scientific. Millipore water (18 M Ω) was used to prepare eluents. Standard sugars were analytical grade. Isomalto-oligosaccharides and low molecular weight dextran (11,500Da) were from Sigma. 1-kestose (1-kestotriose; GF₂), Nystose (1,1-kestotetraose; GF₃) and 1^F- β -fructofuranosylnystose (1,1,1-kestopentaose; GF₄) were generously donated by Dr. Takahisa Tokunage of Meiji Seika Kaisha, Ltd. Leucrose (α -1 \rightarrow 5 linked ketodisaccharide) was from Pfiefer and Langen. Raftilose P95TM was a gift from Raffinerie Tirlemontoise, SA, and Actilight 950PTM was a gift from Beghin Say.

Glucose and Fructose

Glucose and fructose concentrations were determined by IC-IPAD using a Dionex (Sunnyvale, CA, USA) BioLC instrument. See Eggleston and Clarke (1997) for the full method. Lactose was used as the internal standard.

IC-IPAD Analysis of Oligosaccharides

Oligosaccharides (mainly 2 to 12 degrees of polymerization) were determined on composite samples, diluted 1g/25 mL then filtered through a 0.45 µm filter. Oligosaccharides chromatograms were obtained using IC-IPAD on a Dionex BioLC instrument. The oligosaccharides were separated on Dionex CarboPac PA-1 guard and analytical anion exchange columns (250 x 4 mm), at ambient temperature (~25 °C). Flow rate = 1.0 mL/min. Eluent conditions were: 100 mM NaOH isocratic (0.0-1.1 min; inject 1.0 min), a gradient of 0 to 300 mM NaOAc in 100 mM NaOH (1.1-40.0 min), and return to 100 mM NaOH (40.1-45.0 min) to re-equilibrate the column. Oligosaccharides (from 100 µl injections) were detected with a PED-2 detector and detector conditions are listed in Eggleston and Clarke (1997). Using a Spectra-Physics SP8880 autoinjector and Dionex Peaknet chromatography software, runs were accumulated of multiple samples and standards, and oligosaccharide were quantitated in reference to raffinose.

Statistical analysis

Pearson correlation coefficients were calculated to investigate relationships among the various measurements using PC-SAS 6.12 (SAS Institute, Cary, NC). Correlations were initially calculated without regard to harvest treatment. Correlation coefficients were also calculated for measured variables for each specific harvest method treatment.

RESULTS AND DISCUSSION

Theoretical Recoverable Sugar

Results for the yield of theoretical recoverable sugar (TRS) per ton of cane are listed in Table 2. Unexpectedly, there were no marked reductions in TRS for any of the treatments over the 72h of storage. Moreover, for green (D) or burned (E) whole-stalk cane left on the heap row or burned whole-stalk cane stored in the greenhouse to simulate transloader stack conditions (F), the TRS of these treatments actually increased with storage time. This is mainly because of the loss of moisture (dehydration) of the stalks and is merely a function of concentration. Irvine (1972) previously stated that sucrose content and/or TRS are less sensitive indicators of cane deterioration than soluble polysaccharides and dextran.

Color Changes

Initial (0h) color for all treatments was mostly associated with “green” leaves and tops (Fig. 1), and was highest in green whole stalks (B and D), particularly in the handcut green standing whole-stalk (B), and green billets (G). “Green” leaves and tops were more limited in the green billets (G) than in the whole-stalks B and D, because the combine harvester is capable of removing some leaves and tops (trash), and this is reflected in the relatively lower color of G to B and D, on storage. Similarly, in a recent factory study on fresh cane billets, Godshall (2000) also repeatedly observed that color is higher in green than burnt billets.

Color formed dramatically in the burnt billets (H) compared to the more stable green billets (G). In burnt billets the increase of color on storage is directly correlated ($R=-0.95$, $P<.05$) with pH decrease and cane deterioration, and the colorant(s) formed could be from the inversion of sucrose, but the exact nature of the colorant(s) needs to be further investigated.

Table 2. Effect of harvest treatment and storage time on theoretical recoverable sugar (trs) values.

Harvest Treatment	TRS			
	0h	24h	48h	72h
A - Net Cane, Whole-Stalk	281A ^a	277A	274A	284A
B - Green Standing, Whole-Stalk	242CD	243CD	245CD	268B
C - Burn Standing, Whole-Stalk	261B	252BC	256B	258C
D - Green Heap, Whole-Stalk	247C	248C	252BC	273B
E - Burnt Heap, Whole-Stalk	259B	257B	277A	281A
F - N Day Old Stored Burnt Whole-Stalk		257B	274A	284A
G - N Day Old Stored Green Billet	246C	245CD	247CD	247D
H - N Day Old Stored Burnt Billet	237D	236D	239D	241D

^a Capital letters represent significant differences between treatments within each storage time

pH Decreases

Although organic acids are produced from the degradation of sugars on cane deterioration causing a reduction in pH, pH is not considered as a sensitive measure for deterioration because the buffering capacity of the juice reduces this pH change on deterioration. Nevertheless, there was a marked difference in pH decrease on storage between the billeted and whole-stalk canes (Fig. 2), and similar differences were observed by comparing titratable acid results (not shown). In the whole-stalk cane (A to F) pH was generally stable on storage (Fig. 2), whereas for both green (G) and burnt billets (H), deterioration, as indicated by the decrease in pH, particularly set in after 24h storage and continued to 72h, and the rate of pH decrease was worse in the burnt billets (H).

Glucose and Fructose

Even initially (0h), glucose and fructose were dramatically higher in the green (G) and burnt (H) billeted cane than in the whole-stalk cane (A to F), and these higher concentrations were maintained across the 72h storage period (Figs. 3a and b). This is not surprising as the multiple cuts to produce billets from the whole-stalk provides multiple wound sites and associated cell rupture, which allows more sucrose inversion to occur and produce glucose and fructose. For the whole-stalk samples,

green standing (B) and green heap (D) whole-stalks also had higher initial (0h) glucose and fructose (Figs. 3a and b), further indicating that the green leaves and tops contribute most to glucose and fructose concentrations.

In the control handcut field canes (A to C) and soldier harvested canes (D to F) glucose and fructose decreased more on storage after the first 24h, compared to the billeted canes (G and H; see Figs. 3 and b).

Dextran

Dextran concentrations by both the Rapid Haze and ASI-II methods are shown in Figs. 4a and b, respectively. Dextran formation was markedly greater and more rapid in the billeted cane compared to the hand cut and soldier harvested whole-stalk canes (A to F). Furthermore, dextran formed more rapidly and extensively in burnt billets (H) than green billets (G) and this was also reflected in a concomitant greater increase in turbidity levels (results not shown). This is not surprising as the multiple cut ends and associated cell rupture in the billeted cane releases more sucrose for *Leuconostoc* bacteria to utilize and form dextran. Moreover, burning causes even further cell rupture, which explains why dextran formation was even greater in the burnt billeted cane. These results are in agreement with Ravelo et al (1991b) who proved with statistics that the formation of dextran, compared with total oligosaccharides and ethanol, forms more rapidly in burnt billets than green billets and hand-cut cane. Haze dextran (Fig. 4a) in the billeted cane samples appeared later than the ASI-II dextran, that is after 48h of storage. This is because Haze dextran only measures high molecular weight MW dextran, whereas the ASI-II method measures both low and high MW dextran, although there was still a strong correlation ($R=0.98$, $P<.0001$) between the two methods.

Oligosaccharides

Like the dextran polysaccharide, oligosaccharides directly impact factory processing efficiency. Traditional factory clarification processes are incapable of removing all polysaccharides, and also all oligosaccharides (Eggleston, 2000), and oligosaccharides can subsequently interfere with crystallization, deforming the crystal shape, and they end up in the raw sugar causing refining problems too. Oligosaccharides are known to form in deteriorated cane between cut and crush delays, but their formation has been usually attributed to microbial activity (Ravelo et al, 1991a) and enzymic activity (Morel du Boil, 1995). However, kestose oligosaccharides, which can form from enzymic activity in the cane, are also degradation products from the inversion of sucrose and are, therefore, formed from chemical reaction activity as well. Eggleston et al (1997) previously observed that oligosaccharide products are formed from sugar degradation reactions across various unit processes in the sugar industry.

In this study oligosaccharides up to approximately 12 degrees of polymerization (DP) were detected using ion chromatography with integrated pulsed amperometric detection (IC-IPAD) with a strong sodium hydroxide/sodium acetate gradient method. The column used can tolerate high overload concentrations of sucrose in the juices and still detect low concentrations of oligosaccharides, and is also capable of separating oligosaccharide isomers. Fig. 5 illustrates that juice from fresh and deteriorated burnt billeted cane, as well as a typical Louisiana raw sugar have a wide spectrum of IC-IPAD peaks. The major oligosaccharides from the kestose family - 1-kestose (GF₂), 6-kestose (GF₂), neo-kestose (GF₂), nystose (GF₃), and kestopentaose (GF₄) and kestohexaose GF₅ isomers, as well as oligosaccharides associated from the formation of dextran by dextransucrase in *Leuconostoc*

mesenteroides (isomaltotriose, isomaltotetraose, leucrose and palatinose) were identified by comparing retention times with standards and by spiking with standards.

Formation of oligosaccharides on storage/delay time

Initially (0h) there were no marked differences in oligosaccharide profiles for all the eight harvest treatments, which reflects the freshness of all the samples. This also suggests that initially, when the field cane is cut, freshness is more important than harvest method. This has considerable consequences at the factory: as long as billeted cane is transported to the factory quickly on the day it is harvested, no worse deterioration problems should be encountered to those in fresh-cut soldier harvested cane.

In comparison, however, there were marked differences in formation of oligosaccharides on storage/delay time, particularly between the whole-stalk (A to F) and billeted (G to H) cane juices, and example IC-IPAD chromatograms are shown in Fig. 6. Typical oligosaccharide profiles across 0 to 72h storage/delay time for the hand-cut green standing (B) and soldier harvested green heap (D) whole-stalk canes are shown in Figs. 6a and b, respectively, and quantitative results of the major oligosaccharides are further illustrated in Figs. 7a and b. Although both B and D harvest treatments showed a slight increase in the major kestoses (1-, 6- and neo-kestotrioses) after 24h storage (Figs. 7a and b), which was probably due to an environmental stressor in this study, no marked differences were observed across the 72h storage time. Furthermore, very little amount of dextran oligosaccharides were found and these did not increase on storage (Figs. 7a and b), which agrees with the dextran results (see Fig. 4).

In strong contrast, for both green (G) and burnt (H) billeted cane, oligosaccharides formed rapidly across the 72h storage period, with greater deterioration occurring more rapidly in the burnt than green billets (see IC-IPAD chromatograms in Figs. 6c and d and quantitative results in Figs. 7c and d). Marked deterioration occurred in the billet juices even during the first 24h of storage (Figs. 6c and d and Figs. 7c and d) and deterioration oligosaccharides included kestoses and dextran oligosaccharides, which is in agreement with the increase in ASI-II dextran observed after 24h in the billeted cane (see Fig. 4b). In the burnt billet juices particularly (Figs. 6d and 7d), 1-kestose increased steadily up to 48h storage and then plateaued.

The dextran oligosaccharide, isomaltotriose, increased more dramatically in burnt than green billets and was at higher levels after 48 and 72h of storage (compare Figs. 7c and d). Furthermore, leucrose, a secondary product of the formation of dextran from sucrose by *Leuconostoc mesenteroides* (Stodola et al, 1952) was visible in green and burnt billeted cane after 24h storage (Figs. 6c and d), and was at higher levels after 48 and 72h of storage in the burnt billets. This confirms the low and high MW dextran formation results (Fig. 4b). The higher MW kestoses: nystose (GF₃), GF₄ and GF₅ isomers, were also greater in burnt billeted cane, on storage, indicating further that more extensive deterioration occurred in the burnt billet from enzymic and chemical deterioration reactions. Ravelo et al (1991b) similarly observed that total oligosaccharides formed more rapidly in burnt than green billets, although specific oligosaccharides were not measured and, therefore, the source of the faster deterioration is unclear. Furthermore, Morel du Boil (1995) observed that the major kestotrioses

(GF₂) were formed more rapidly in burnt than green whole-stalk cane during cane delays, but rapid increases did not occur until after 3 days of delay, a situation that occurs infrequently in Louisiana.

It was interesting to note that an unidentified peak denoted "X", near to the 1-kestose peak (Figs. 6c and d) increased dramatically with storage time in the billeted canes and could, therefore, be an excellent indicator or marker of deterioration. This peak may be theandrose (a trisaccharide; Morel du Boil, 1995) and further investigations using a fraction collector and GC-MS/LC-MS are currently being undertaken to identify it.

MAJOR CONCLUSIONS

- ▶ On storage, billeted cane deteriorates earlier and faster than handcut and soldier harvested whole-stalk cane
- ▶ Burnt billeted cane deteriorates faster than green billeted cane on storage, as indicated by a greater decrease in pH, and a greater increase in color, invert, dextran and oligosaccharide concentrations
- ▶ Initial cane color is mostly attributable to the amount of "green" leaves and cane tops (trash)
- ▶ Billeted cane can deteriorate rapidly, especially after the first 24h of storage (although it also occurs before 24h), which reinforces the need for factories to quickly process freshly cut billeted cane
- ▶ GF₄ and GF₅ kestoses have been identified in deteriorated cane, and are present in raw sugars

DISCUSSION ON OPTIMUM HARVEST AND STORAGE METHODS

As industries increase their level of mechanization, lower cane quality is often observed with an increase in trash; however, overall efficiency is normally improved and costs are often reduced (Richard, 1999). This study highlights the real need for mechanically harvested cane delays (cut to crush time) to be minimized to reduce dextran and oligosaccharide loads at the factory and prevent future processing problems, and this is especially true for billeted cane, in particular burnt billeted cane. Furthermore, for billeted cane, especially burnt billeted cane, there is less than a 24h time window from cutting to crushing, which allows factories to minimize possible processing difficulties associated with dextran and oligosaccharide formation.

Factors other than cane quality/deterioration chemistry dominate the decision to burn or not to burn the cane (cane burning is thought important in order to effectively remove trash) (Clarke and Legendre, 1996). However, in Louisiana and other areas, there are growing environmental concerns associated with the burning of cane, especially near populated areas, and green cane harvesting has been increasing throughout the world (Richard, 1999). This study highlights the problems associated

with color when harvesting green cane, but this could be overcome effectively by utilizing technologically more advanced hot or intermediate lime clarification processes in preference to the more conventional cold liming process often in use.

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Fig. 1. Harvest method and storage effects on color

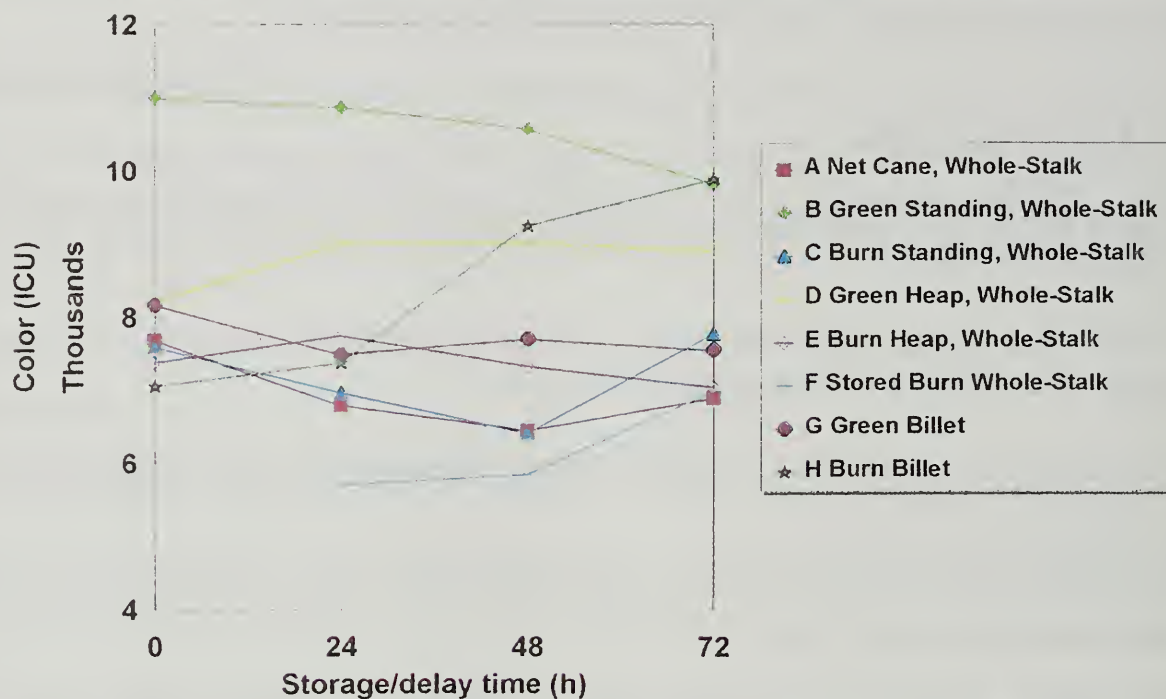


Fig. 2. Harvest method and Storage effects on pH

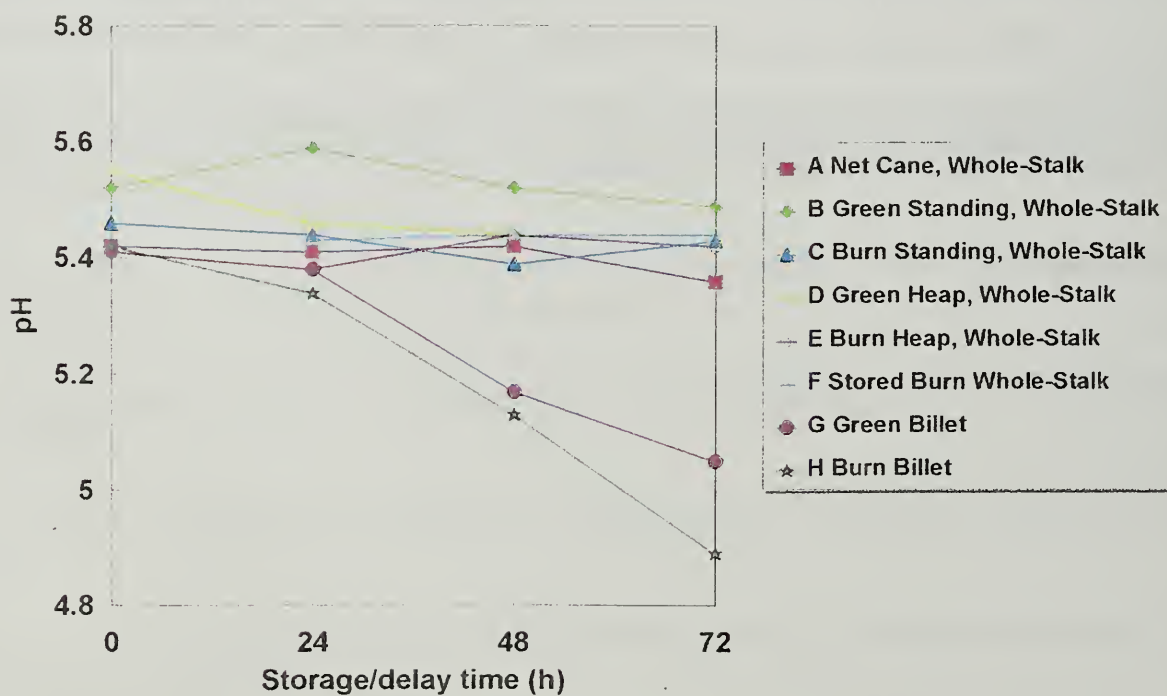


Fig. 3a. Harvest method and storage effects on glucose

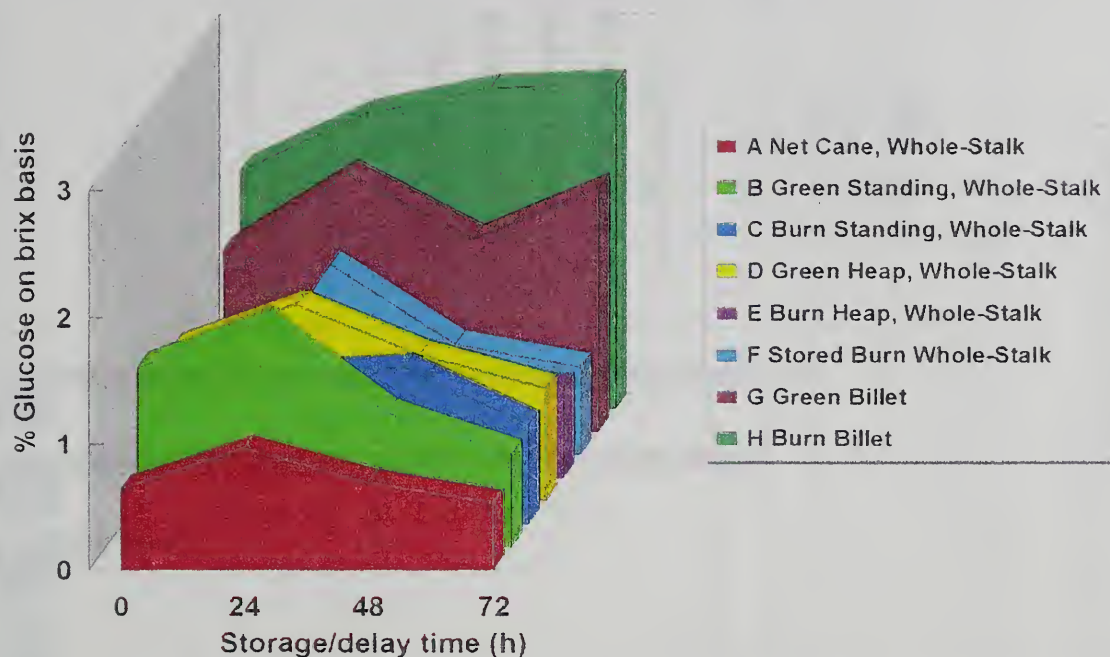


Fig. 3b. Harvest method and storage effects on fructose

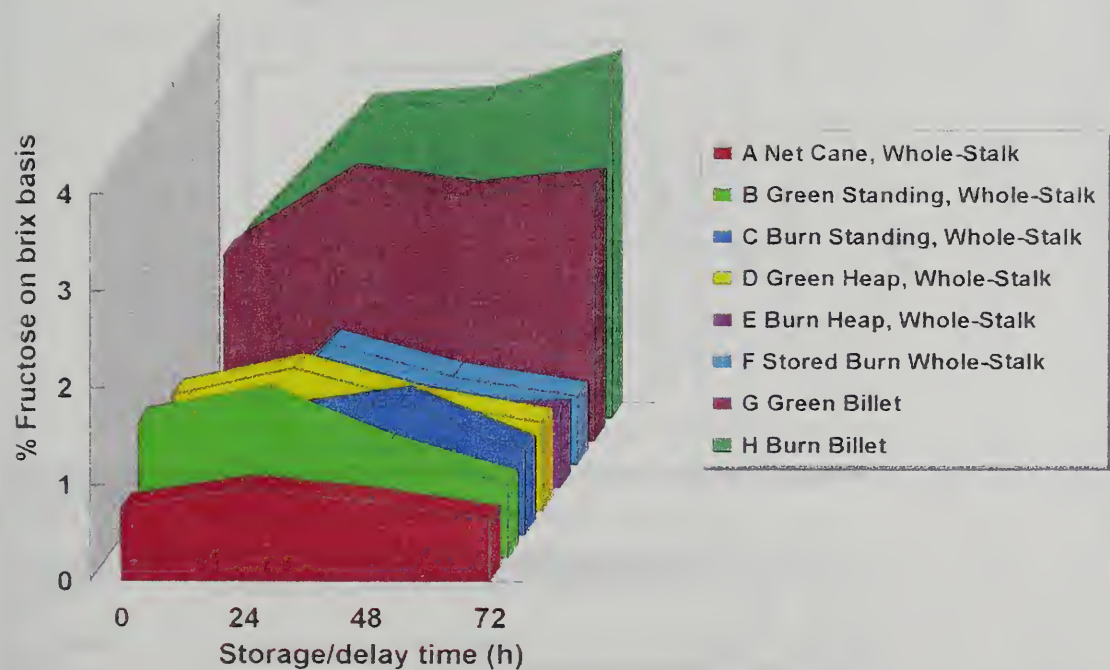


Fig. 4. Harvest method and storage effects on a) Haze dextran and b) ASI-II dextran

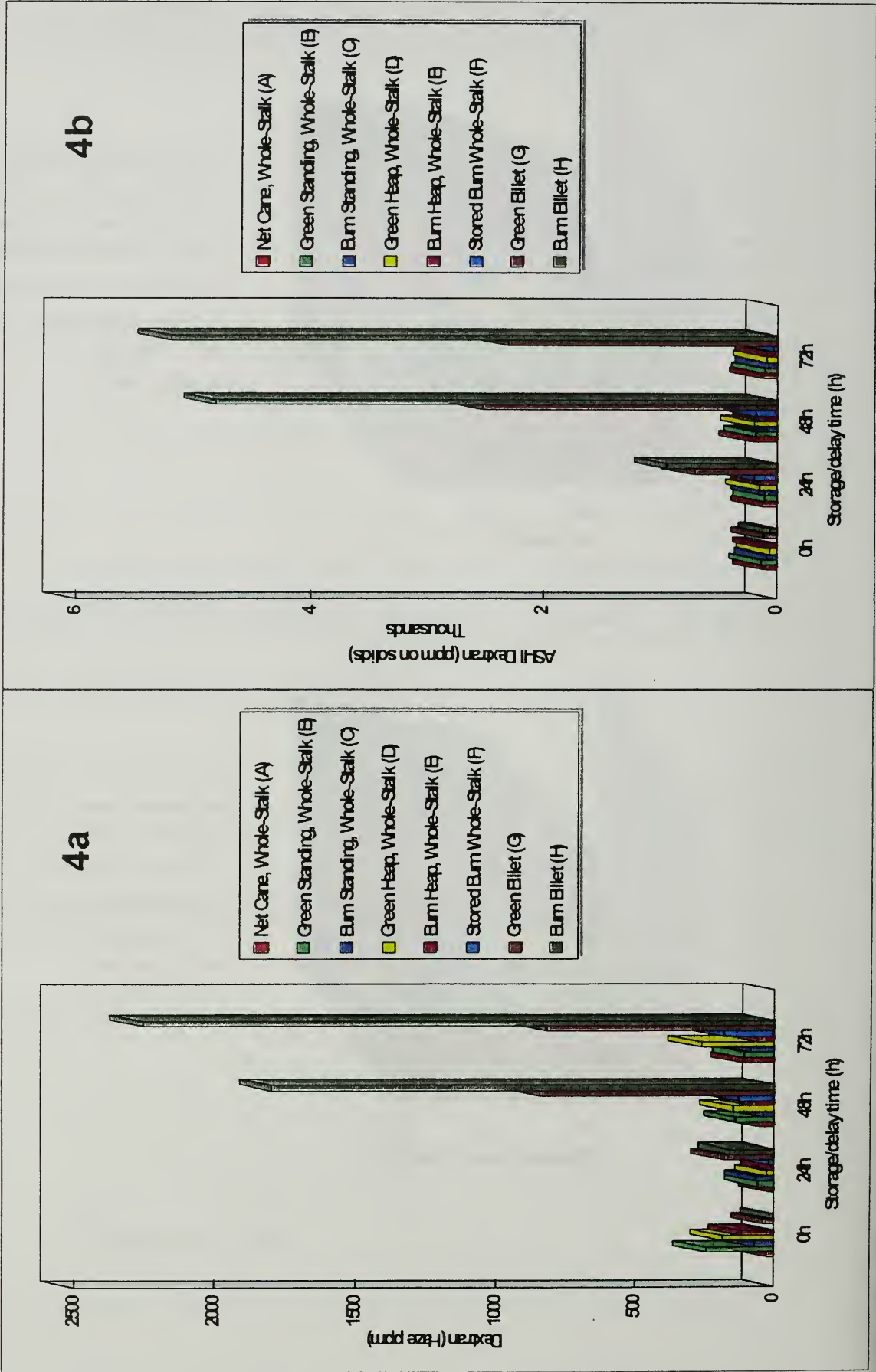


Fig. 5. IC-IPAD chromatograms showing oligosaccharides in cane juices and raw sugar

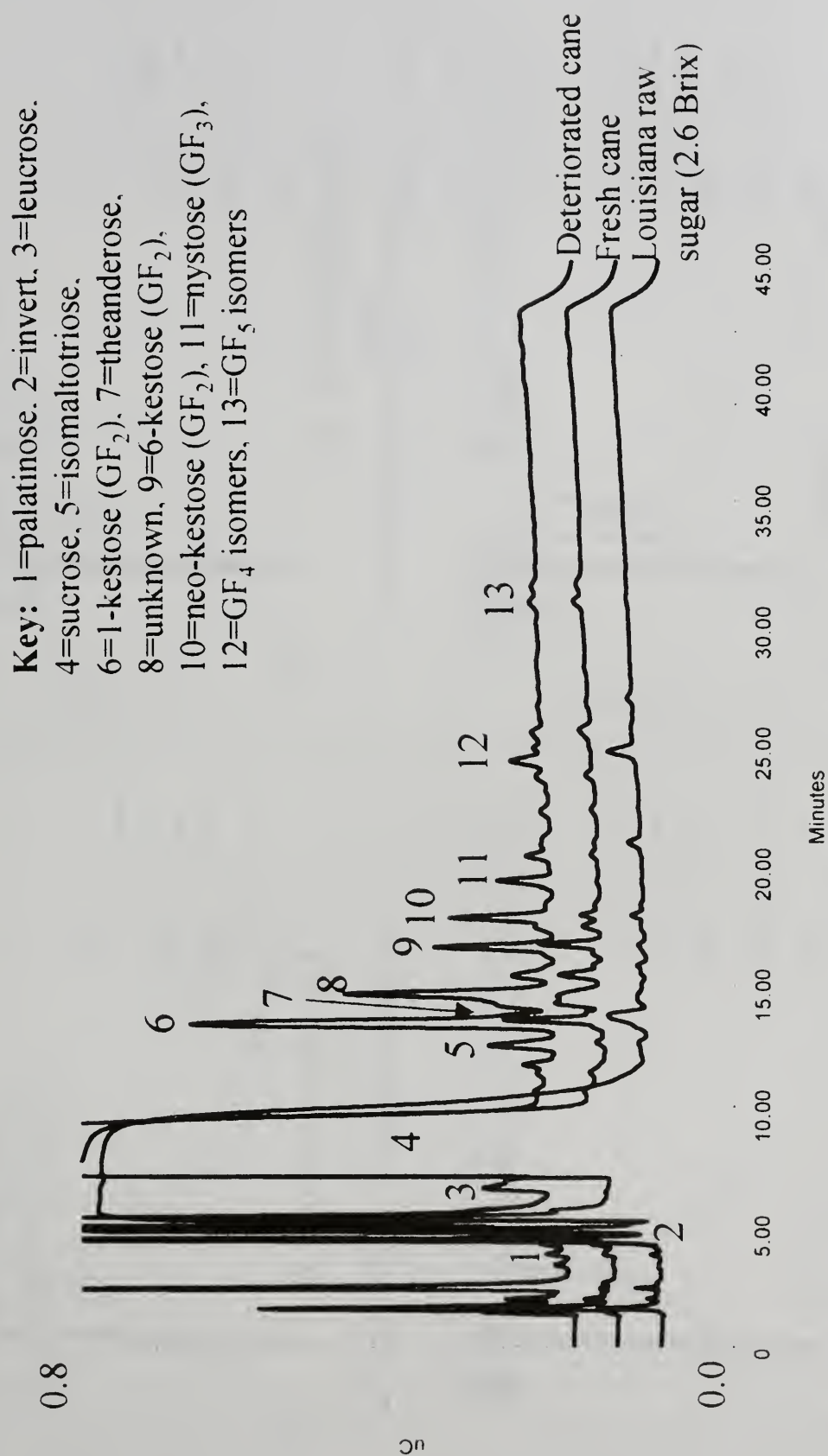


Fig. 6. Example oligosaccharide chromatograms on storage (Brix adjusted Cane Samples)

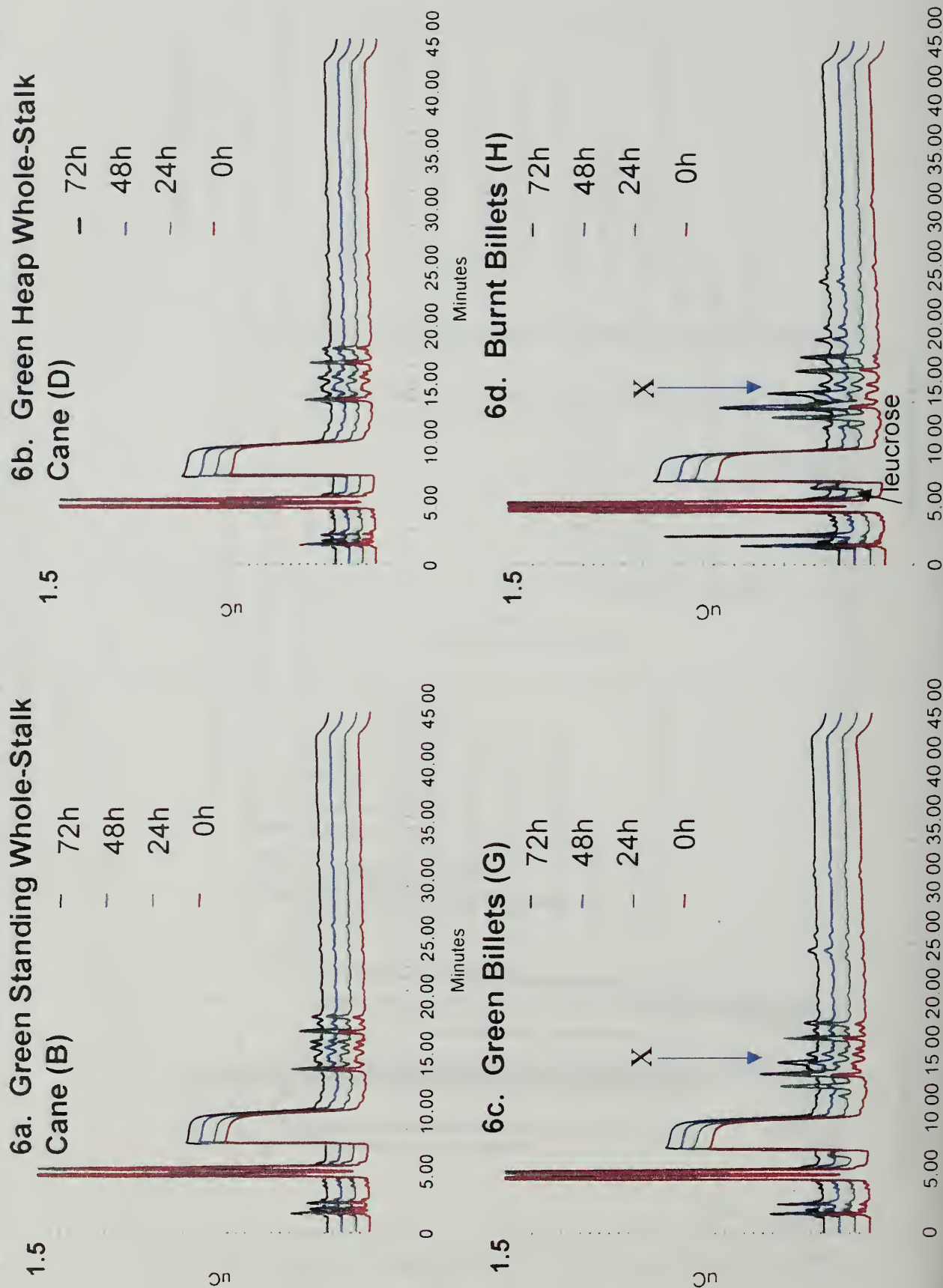
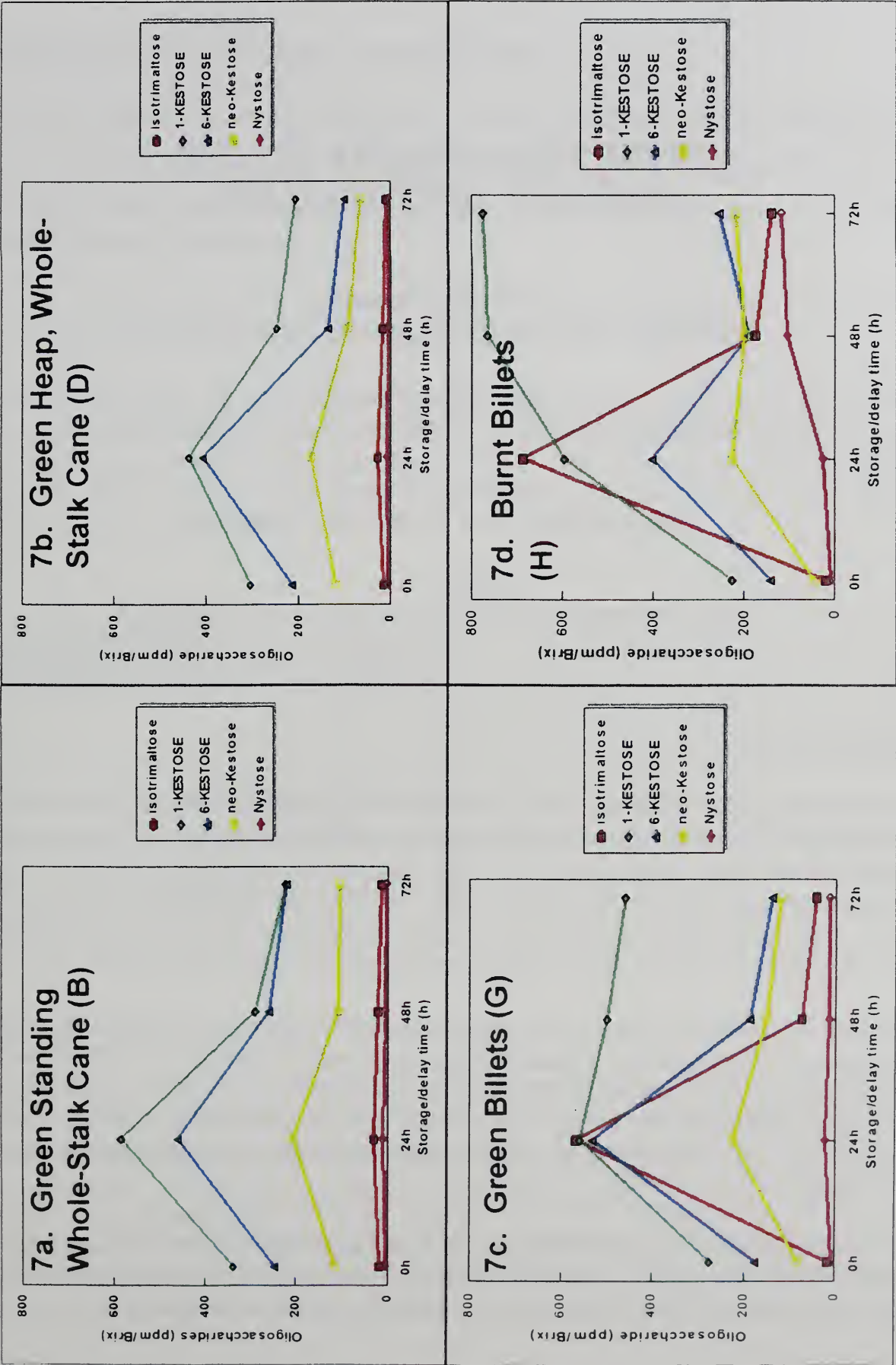


Fig. 7. Oligosaccharide formation on storage



EFFECT OF HARVEST SYSTEM ON CANE JUICE QUALITY

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INTRODUCTION

The Louisiana sugarcane industry is in the process of switching from whole stalk harvesting (soldier harvesting) to billet harvesting (combine harvesting) and from mostly burned cane to mostly green (unburned) cane. These changes have to do with environmental pressures, economies of scale, and new, more recumbent varieties that are more effectively harvested by a combine harvester. There has been a perception that the quality of cane juice is lower when it is combine harvested, but systematic tests have not been done to determine if there are differences in cane juice quality.

The research reported here is part of two larger studies undertaken in 1999 by the Louisiana Sugar Cane League, in cooperation with Sugar Processing Research Institute, Inc., U.S. Department of Agriculture Sugarcane Research Unit and Southern Regional Research Center, and Audubon Sugar Institute of Louisiana State University. The studies were designed to test the effect of the harvest system on the quality of the cane juice and to test the effect of stale cane/deterioration on the quality of cane juice.

The involved institutions analyzed different cane juice parameters in order to obtain a wide range of indicators of cane juice quality. The results reported in this presentation will concentrate on color, turbidity and polysaccharides as they were affected by the various treatments.

Factors that Affect Cane Juice Quality -- a Brief Review.

There is a two-fold objective in cane harvesting and processing: to maximize sucrose and to minimize impurities. To maximize sucrose, high yielding, disease resistant varieties are used, field and processing conditions are optimized and microbiological contamination is controlled. To minimize impurities, optimized field practices are the most important, such as minimizing leaves, tops, and mud in the cane and bringing in fresh cane.

Legendre, et al. (1999) reviewed developments in sugarcane agriculture that affect processing. Delgado (1977) discussed the effect that burning has on the quality of cane juice.

It is important to minimize the impurities in the cane juice because, not only do these impact processing, but they will also impact the final quality of the raw sugar. Impurities will transfer more or less into the raw sugar crystal, depending on their nature, and it is safe to say that between 10-50% of incoming impurities will transfer into the raw sugar. Some typical ranges are shown in Table 1, based on many years of research at S.P.R.I.

Table 1. Transfer of impurities from juice to raw sugar.

Juice Constituent	% in Raw Sugar
Color	10 - 20
Starch	30 -50
Dextran	30 -50
Ash	5 -15
Polysaccharides	20 -30

Many factors affect cane juice quality, including:

● **Stale cane.** This is perhaps one of the most significant contributors to problems in processing. Stale cane can develop dextran, invert sugar, and sucrose loss. There is a lot of interest in developing a test for stale cane or sucrose loss. Research in South Africa indicates that 1-2% sucrose is lost for each day the cane is left cut in the field. They have experimented with using ethanol as an indicator of cane deterioration, estimating that 1000 ppm of ethanol on juice solids correlates to a 2% loss of sucrose. Dextran is another indicator of sucrose loss, and researchers at Audubon Sugar Institute have estimated that 250 ppm dextran in juice (haze method) can lead to a 0.3% sucrose loss. Eggleston has researched oligosaccharides as possible indicators of sucrose loss.

● **Immature cane.** Aconitic acid, invert and starch are higher in immature cane.

● **Ragged vs clean cutting of cane during harvesting.** Ragged cuts lead to diffusion losses and microbial infections.

● **Mud and trash in cane.** These lead to an increased load of particulate matter, color, turbidity and polysaccharides in the cane juice, putting a greater burden on the clarification and leading to greater chemical and energy usage (Legendre, *et al.*, 1996). Color contributed by leaves can increase the over-all color by as much 50%. Table 2 compares juice from clean stalks to juice from leaves.

Table 2. Comparing clean stalk juice to juice from leaves and tops

Component	Clean Stalk Juice	Juice from Tops
Brix	18 - 22	7 - 10
pH	5.44	5.34
Color	6,280	77,660
Indicator Value (I.V.)	5.54	2.73
Polysaccharide, ppm	1,352	20,044
Starch, ppm	710	4,037
Filtration rate (10ml/0.45μ)	15 min	130

● **Weather.** The grower has no control over the weather, but it can be a large factor in poor quality cane, as when a hurricane or storm leaves the cane recumbent and twisted on the ground, or when an early freeze come along. Drought and excess rain both have an impact.

● **Soil type.** High clay soils are more “sticky” than sandy type soils and can result in dirty cane.

● **Diseases.** Diseases always result in lost sugar and sometimes in increased carbohydrate (polysaccharide) content, higher viscosity, and inversion of sucrose. These are mostly controlled by using disease-resistant varieties.

● **Varietal differences.** Besides having significant varietal differences in sucrose content, maturation date, and disease resistance, varieties can differ as much as 3-fold in clean cane juice color and 6-fold in starch content.

● **Time of year.** Research by Lionnet (1988, 1991) in South Africa has shown that cane juice quality is better in the middle of the crop season than either the beginning or the end, and that the time of year was a stronger indicator of raw sugar quality than any other factor. Godshall and Legendre (1988) showed that phenolics in juice increased significantly as cane matured.

● **Grower practices.** These relate to issues such as how long the farmer has left the cane in the field before bringing it to the mill, whether he burns or harvests green cane, whether he harvests whole stalk or billet cane, how well trash is removed, whether cuts are clean or ragged, and cultivation practices.

MATERIALS AND METHODS

Test of Harvest System -- St. Martinville Experiments

Sugar Processing Research Institute, Inc., participated in the 1999 study of harvest systems in Louisiana. The test was designed to determine the effect on cane juice quality of soldier harvested cane versus combine harvested cane and of green cane versus burned cane and of dry weather versus wet weather. Harvest tests took place on October 13, 14, and 15 and on December 22 and 23, 1999.

Briefly, in October, three growers participated, providing composites of 8-9 core samples of green billets, burned billets, burned whole stalk cane and hand cut clean cane controls. Sampling was as follows:

- October 13 - Green billets (GB)
Green billet mixed juice (MJ-GB)
Clean cane control, 15 hand cut and cleaned stalks (CCC)
- October 14 - Burned billets, standing cane burned the day before (BB)
Burned billet mixed juice (MJ-BB)
- October 15 - Burned whole stalk on heaprow 3 days (BWS)
Burned whole stalk mixed juice (MJ-BWS)
Green whole stalk special samples, 2 growers, 2 varieties (GWS)

In December, following heavy rainfall earlier in the week, 7 loads were sampled for each treatment, and 3-4 core samples were composited. The burn may not have been complete because of the wet nature of the cane. Sampling was as follows:

- December 22 - Green billets (GB)
Green billet mixed juice (MJ-GB)
Green whole stalk (GWS)
Green whole stalk mixed juice (MJ-GWS)
Hand cut clean cane control (CCC)
- December 23 - Burned billets, burned the day before (BB)
Burned whole stalk, burned the day before (BWS)
Burned whole stalk mixed juice (MJ-BWS)

Deterioration Test -- Rebecca Farm Experiments

This experiment was designed to test the differences between deterioration rates of combine harvested, hand harvested and soldier harvested green and burned cane, over a period of 5 days. The study involved several research groups, with S.P.R.I. measuring polysaccharides, color, pH and ash.

One half of a field approximately 12 acres in size was burned and the other half was left green. Over a period of 5 days, one truckload each of burned billets and green billets were harvested. Unfortunately, none of these samples were delivered to S.P.R.I.

Hand sampling was also done. On each day for five days, four 15-stalk samples were hand harvested from both the green and burned cane supplies, topped at the uppermost dewlap. A third green harvest cane sample was cut, topped at the uppermost hard joint, and stripped to remove all leaves prior to crushing.

Also, on the first day of the experiment, a soldier harvester cut an adequate cane supply (approximately 100 feet of cane) on either side of the field prior to burning. After one side of the field was burned, 15-stalk bundles were prepared of both green and burned cane supplies. Additionally, samples of a stripped, unburned cane supply were prepared.

The treatment codes were the following:

- Hand harvested (daily), green cane, with side leaves (HGL)
- Hand harvested (daily), green cane, stripped of leaves (HGC)
- Hand harvested (daily), burned cane, with side leaves (HBL)
- Hand harvested (daily), burned cane, stripped of leaves (HBC)

- Soldier harvested (day 0), green cane with side leaves, left on heap up to 5 days (SGL)
- Soldier harvested (day 0), green cane, stripped of leaves, left on heap up to 5 days (SGC)
- Soldier harvested (day 0), burned cane, with side leaves, left on heap up to 5 days (SBL)
- Soldier harvested (day 0), burned cane, stripped of leaves, left on heap up to 5 days (SBC)

- Combine harvested (day 5), burned billets, processed 4 hours later (BB-4)
- Combine harvested (day 5), burned billets, processed 6 hours later (BB-6)
- Combine harvested (day 5), burned billets, processed 8 hours later (BB-8)

Cane juice samples intended for analysis at S.P.R.I. were briefly boiled to inactivate starch degrading enzyme (amylase) in the juice in order to obtain a true starch value. The samples were then immediately frozen and transferred frozen to S.P.R.I. laboratories. Samples were further composited at S.P.R.I., to decrease the large number of samples.

All samples were analyzed for total polysaccharides, dextran, starch, pH, ash, and color. The color indicator value (I.V.) was determined on the first set of St. Martinville samples, and turbidity and invert (by chromatography) were determined on the St. Martinville samples and not the Rebecca Farm (deterioration) samples.

RESULTS AND DISCUSSION

Harvest Method -- St. Martinville Test

Figures 1-7 show the mean results of harvest method on ash, color, dextran, invert, polysaccharides, starch and turbidity. Ash, dextran, invert, polysaccharides and starch decreased from October to December, while color increased. Because the changes were uniform, it was still possible to average the results from the two months, as shown in the figures. These values reflect the changes that occurred in the cane as it matured.

Tables 3 and 4 compare the means of total polysaccharides, dextran, starch, color, turbidity and pH for October and December. Statistical analysis was done only for the data in October, and green whole stalk (GWS) was not included in the statistics since different farmers produced it, and it was not included as part of the test for October. It was, however, part of the test in December. Significant differences could be noted between the clean, hand-cut cane and the other harvest methods. Additionally, color of green whole stalk cane was very high; turbidity of green billets and green whole stalk cane was much higher than all other harvest methods, and green billets and green whole stalk cane had consistently higher polysaccharides. Green billets had consistently higher invert values than the other treatments. Starch tended to be inconsistent and quite low in some samples. Since starch was high in the clean hand cut cane and very consistent, and this is a high-starch variety, we felt that the delays between coring the sample and compositing it and then heating it, contributed to enzymatic decrease of the starch content in the juice. The mixed juice tended to be higher and more consistent, again because the delay to heating the juice was less, so these values were taken as typical of the respective harvest method. Nevertheless, no effect of harvest method could be noted on starch content.

Table 3. Comparison of means for October and December (Polysaccharide parameters)

Harvest Method	Total Polys		Dextran		Starch	
	Oct	Dec	Oct	Dec	Oct	Dec
CCC	4875b	4081	1677b	1366	1518a	1041
GB	6825a	5260	2414a	1672	999ab	741*
BB	5778ab	3823	1966ab	1593	1245a	821*
BWS	5238b	4417	2154ab	1523	624b	1182*
GWS	7850 [‡]	6326	3034 [‡]	1942	1072	838*

* Mixed juice results mostly or exclusively; other values were extremely low and variable.

[‡] These data from special samples from 2 growers, not included in statistical test.

Results with the same letter are not significantly different at $\alpha = 0.05$.

Mixed juice data are included in data for statistical analyses, not the other means.

Green whole stalk (GWS) was not statistically sampled in October; result represents special samples.

Table 4. Comparison of means for October and December (Color parameters)

Harvest method	Color		Turbidity		pH	
	Oct	Dec	Oct	Dec	Oct	Dec
CCC	5700b	7576	51,168c	72,447	5.30b	5.28
GB	8097a	9631	130,857a	152,445	5.53ab	5.45
BB	8400a	7938	76,469bc	79,503	5.45ab	5.24
BWS	7700a	8401	95,750b	46,093	5.71a	5.52
GWS	9625 [†]	10,395	183,750 [†]	71,692	5.55	5.46

Results with the same letter are not significantly different at $\alpha = 0.05$.

CCC = Clean cane control

GB = Green billets

BB = Burned billets

BWS = Burned whole stalk

GWS = Green whole stalk

Deterioration Study -- Rebecca Farm Experiments

Figures 8-11 show the results of the deterioration study on the levels of ash, color, polysaccharides and dextran in the soldier harvested cane compared to the burned billeted cane. The value for the burned billeted cane was the mean of those processed 4, 6 and 8 hours following billeting. (The clean cane results are not shown.)

In general, burned billets fell within the range for soldier harvested cane in total polysaccharides and were lower in dextran, a common deterioration marker. Burned billets were unusually high in color in this study, whereas in the St. Martinville study, burned billets were not significantly different from other harvest methods, and tended to be on the lower end, especially compared to green cane. This could be an anomalous result, as it would seem unusual that the color would increase so much compared to 5-day standing burned cane. However, further research would have to be done to confirm this one way or the other.

Using dextran as the marker, deterioration was clearly evident on day 5 for all harvest methods. Looking at the increases in dextran and polysaccharides on day 5, it appears that burned cane deteriorates faster, probably due to the loss of protective factors.

Indicator Value (I.V.)

The I.v. is the ratio of color at pH9/pH4, and is an indication of the pH-sensitivity of the color, and an indirect indication of the free phenolics in the juice. Because of the time involved with the analysis,

this parameter was only analyzed for the October St. Martinville (havest system) study. Statistical analysis showed the following results (means with the same letter are not significantly different):

<u>T-Group</u>	<u>Mean</u>	<u>Harvest Method</u>
A	6.92	Clean cane control
A	6.53	Burned billets
B	4.48	Green billets
B	4.09	Burned whole stalk
---	4.32	Green whole stalk

These results show that the I.V. is lower in juice from green cane, either billeted or whole, whereas the burned billets were indistinguishable from the clean cane control juice results. The burned whole stalk cane also had a lower I.V. In earlier studies at SPRI, it was noted that the I.V. of juice from clear, hand cut stalks of known varieties, trimmed below the growing point, was in the range of 3-5, so these results are in line with those findings. In the same studies, it was found that juice from leaves alone had a very low I.V. (cf, Table 2). The presence of leaves in the juice lowers the I.V. This has implications for the type of colorant that is going into the factory.

Heating versus not heating the juice

Since a portion of the juice was heated to inactivate amylase enzyme, to prevent breakdown of the starch, the question arises as to whether the heating step as (a) caused polysaccharides to precipitate, and (b) caused color to increase. Table 5 compares the results from duplicate analyses on portions of juice that were either heated or not heated.

The results indicate that polysaccharides are slightly decreased, around 2% by heating, and color is slightly increased, about 5%, by heating. These figures are not considered significant since the analytical variation in the method at these high values of polysaccharides and color is in the same range.

Table 5. Effect of heating on total polysaccharides and color in cane juice analysis

Sample	Total Polysaccharide		% Change	Color		% Change
	Not heated	Heated		Not heated	Heated	
1	6063	5989	-1.24	6647	7070	+5.98
2	6074	5776	-5.16	8266	8400	+1.59
3	5031	5034	None	7171	7700	+6.87
Mean			-2.13			+4.81

CONCLUSIONS AND SUMMARY

Conclusions from the St. Martinville Test of Harvest Methods

1. **Total Polysaccharides (TPS):** TPS decreased from October to December. The TPS was lower over-all in burned cane, both billet and whole. Green whole stalk had the highest TPS. concentrations in both months.
2. **Dextran:** Dextran decreased from October to December. Dextran in green cane was higher than in burned cane for both months.
3. **Starch:** Starch decreased from October to December. No effect of harvest could be observed from the data. The amylase enzyme in the juice tended to affect the starch levels depending on the time delay to heating the juice. Over-all, this is a very high starch variety, and it is reflected in the mixed juice.
4. **Color:** Color increased from October to December. In October, there was no significant difference in the color of green billets, burned billets and burned whole stalk. Green whole stalk had much higher color than any of the other treatments.
5. **Turbidity:** The amount of turbidity in cane juice was directly related to green cane. The amount of turbidity in green billets was about double that in burned billets and burned whole stalk cane juice. Green billets produced higher turbidity more consistently.
6. **pH:** There was a slight, but consistent, drop in pH from October to December. There was no difference of pH in any of the treatments.
7. **Ash.** There was no difference among the harvest systems. Ash decreased considerably in December. Also, ash increased in mixed juice, on the average, 11%.
8. **Sugars.** Green billets had the lowest sucrose and the highest invert in both October and December. Burned billets had the highest sucrose and lowest invert in October and fell in the middle range for both sucrose and invert in December. Invert levels were very high in October and dropped significantly in December. Green cane (billeted and whole) had higher invert in December.

To conclude, the biggest differences appeared to be between green versus burned cane, whether it was billeted or not. Green billets tended to be consistently higher in turbidity and invert. Otherwise, green billets were better than green whole stalk cane. Green cane, both billets and whole stalk were higher in total polysaccharides, dextran, color, turbidity and invert. Burned billets were about the same or slightly better than burned whole stalk cane in total polysaccharides, dextran, color and turbidity.

Conclusions from the Rebecca Farm Deterioration Test:

1. Green cane generally had higher polysaccharide, dextran and color than burned cane.
2. For the first four days, soldier harvested cane generally showed no difference in polysaccharides and dextran compared to hand harvested cane.
2. Green soldier harvested cane did not differ from hand harvested cane in total polysaccharides in green cane with and without leaves.
3. On day 5, all types of soldier harvested cane showed increased dextran.
4. On day 5, burned soldier harvested cane, both with and without leaves, had significant increases in total polysaccharides.
5. There were no differences in color between all types of soldier and hand-harvested cane.
6. Cane burned and then billeted on day 5 had greatly increased color compared to soldier and hand harvested cane.
7. Burned billeted cane on day 5 averaged lower dextran than all day 5 soldier harvested cane, although it did increase from 4 to 6 hours.
8. Burned billeted cane on day 5 had elevated total polysaccharide when compared to other harvest methods on day 5, but it was almost identical to day 5 soldier harvested burned cane with leaves (5854 ppm vs 5686 ppm).
9. Based on the observations in No. 7 and No. 8, burned billets fall within the range for soldier harvested cane in total polysaccharides and slightly lower for dextran.
10. Up to day 4, there was no deterioration when using dextran and total polysaccharides as indicators, but deterioration became clearly evident by day 5.
11. It also appears that deterioration was greater in burned cane, possibly because some protective factor(s) were removed by burning.

Again, the biggest differences appeared to be between green versus burned cane, whether it was billeted or not. Burned billets did not show any greater level of deterioration than the comparable 5-day burned whole stalk cane.

SOME FURTHER DISCUSSION

The major question for the growers and processors in Louisiana is harvest method vs freshness of cane. What is the significance of each, and which is most important? This study has highlighted the three issues that affect the cane coming into a factory. These issues are:

1. Cane Quality -- how much trash, leaves and mud are included; maturity; variety;
2. Cane Deterioration -- how fresh is the cane;
3. Harvest Method -- if the above two are optimized (clean, fresh cane), the harvest method should not be an issue.

As billeted cane appears to be the wave of the future, methods to optimize billet handling should be studied and recommended. This is especially critical if farmers are required to harvest only green cane, meaning they will lose the trash removal advantage provided by burning. Some guidelines for handling billets would be:

1. Scheduling -- billets should be as fresh as possible
2. Clean cuts -- ragged cuts contribute to deterioration and increased wash water losses
3. Highest combine fan speed to eliminate max amount of trash without loss of billets
2. Washing -- drum vs. table; amount of water; angle of table
3. Hot or intermediate liming instead of cold liming?

Some practical, and as yet, unanswered questions that merit further research are:

1. What does poor quality cane cost the mill?
2. Is there a test for fresh cane?
3. Is there a test for cane deterioration?
4. How much sucrose is lost for each increment of a deterioration indicator, such as ethanol, lactic acid, dextran, oligosaccharides?

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Figure 1. Effect of Harvest System
On Ash (Oct + Dec)

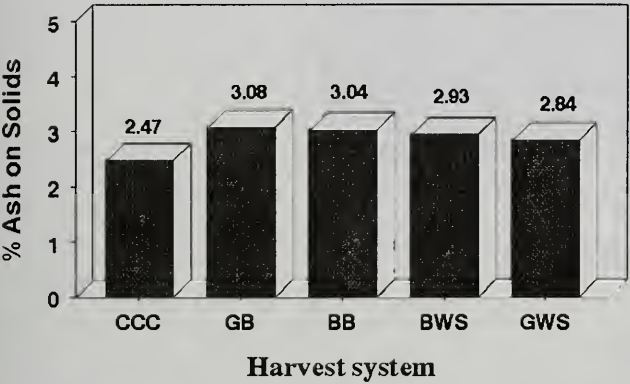


Figure 2. Effect of Harvest System
On Color (Oct + Dec)

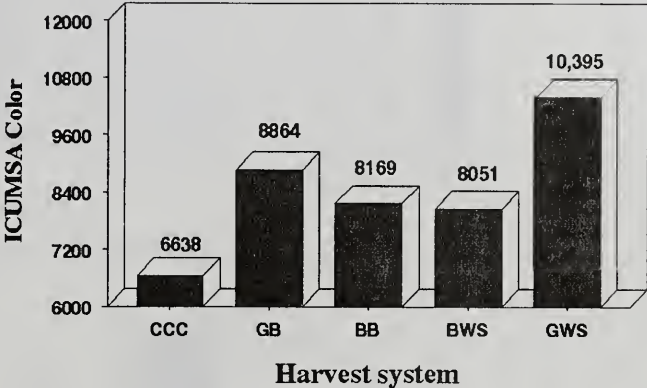


Figure 3. Effect of Harvest System
On Dextran Concentration (Oct + Dec)

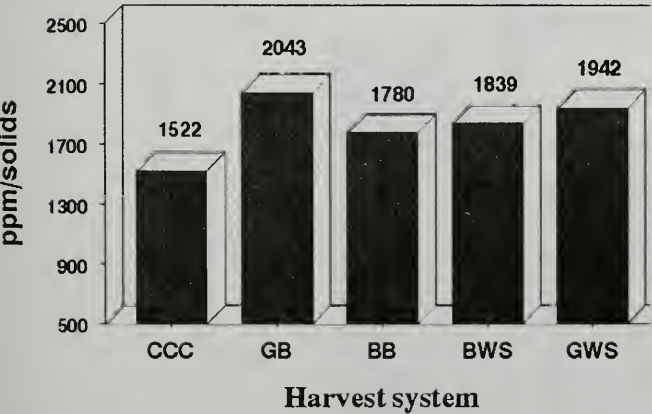
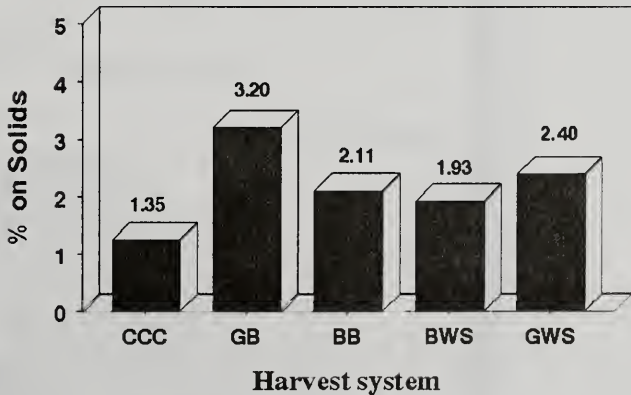
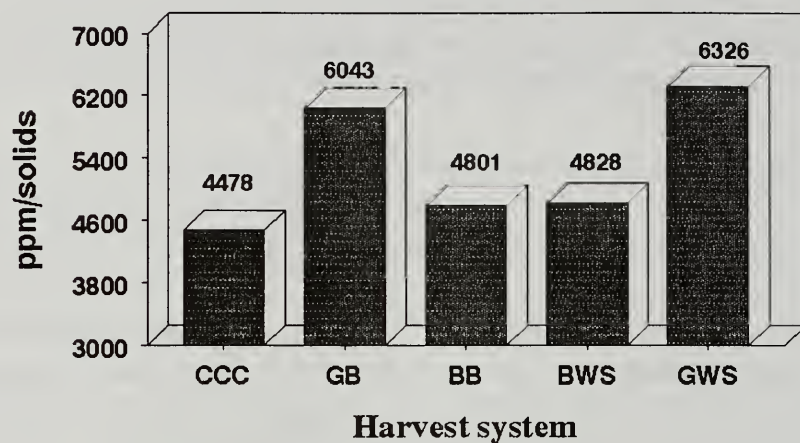


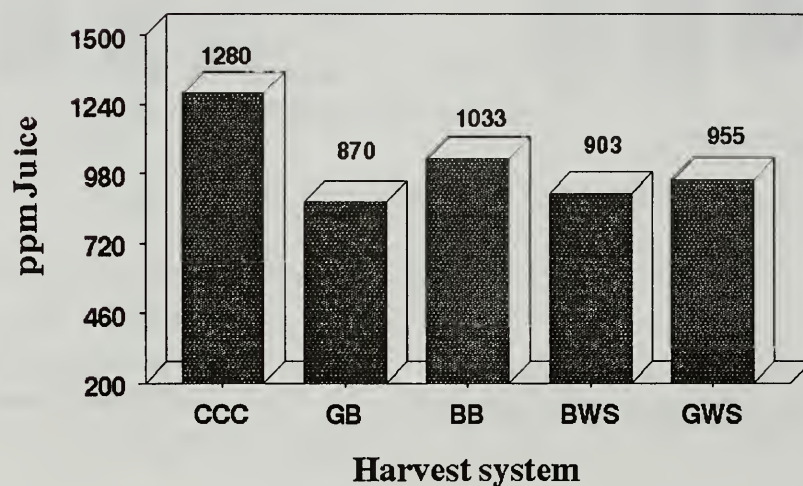
Figure 4. Effect of Harvest System
On Total Invert (Dec)



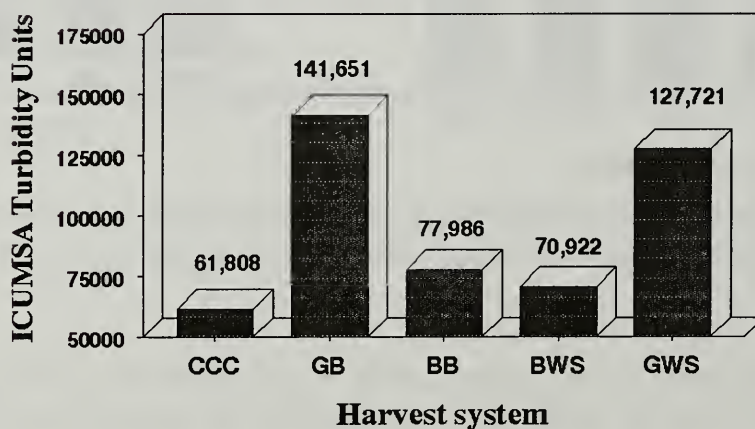
**Figure 5. Effect of Harvest System
On Total Polysaccharides (Oct + Dec)**



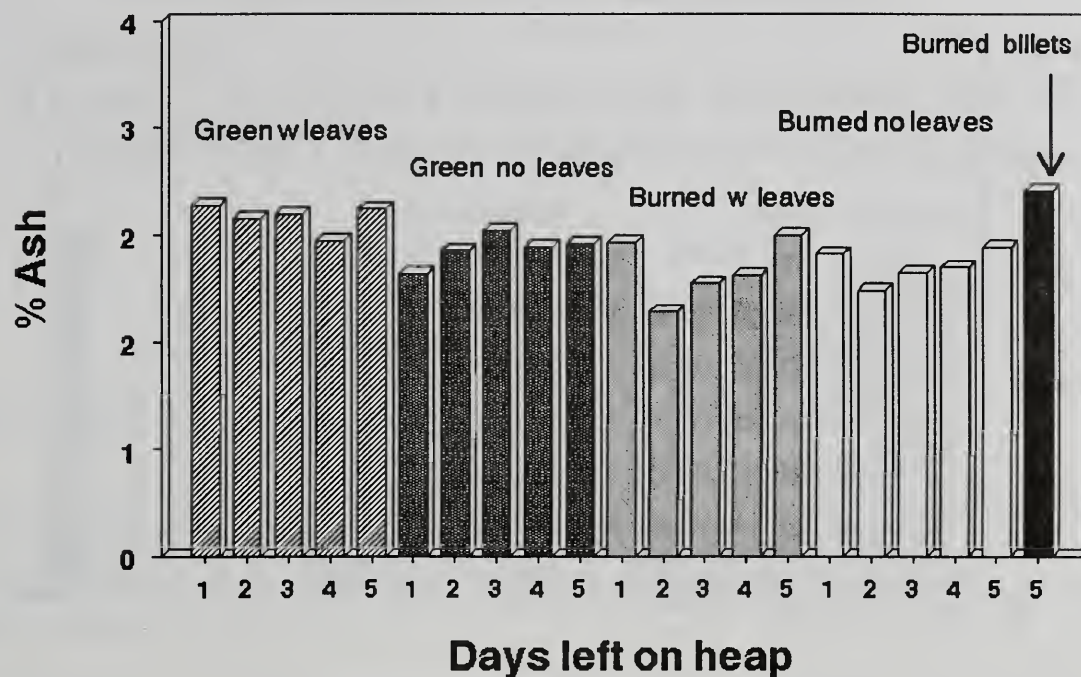
**Figure 6. Effect of Harvest System
On Starch (Oct + Dec)**



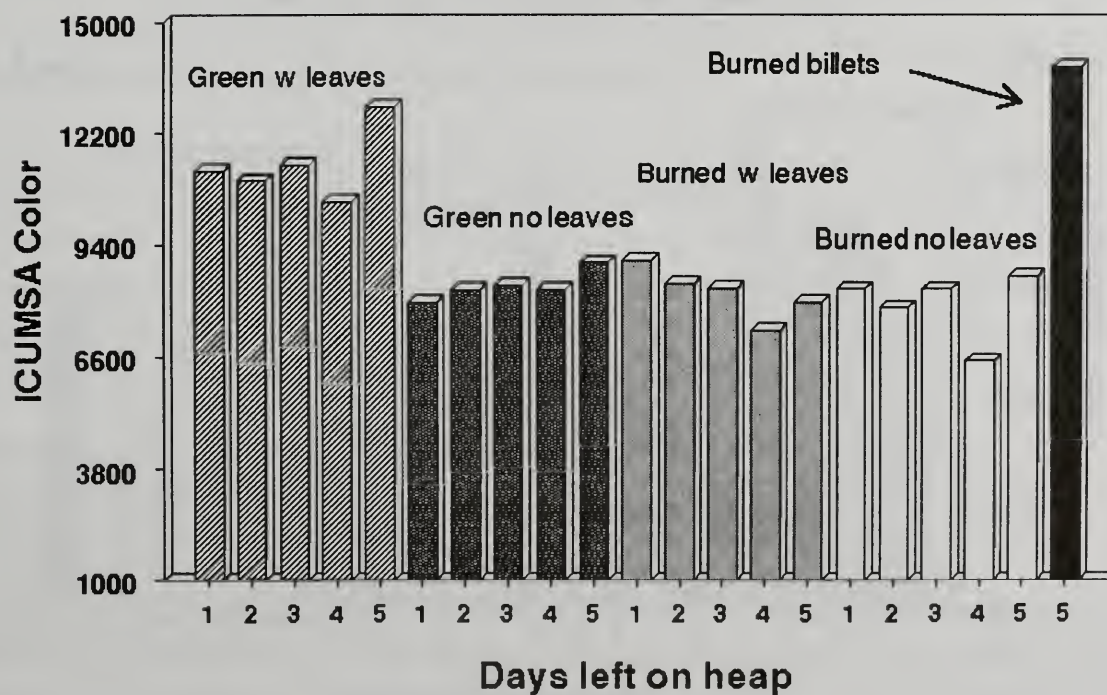
**Figure 7. Effect of Harvest System
On Turbidity (Oct + Dec)**



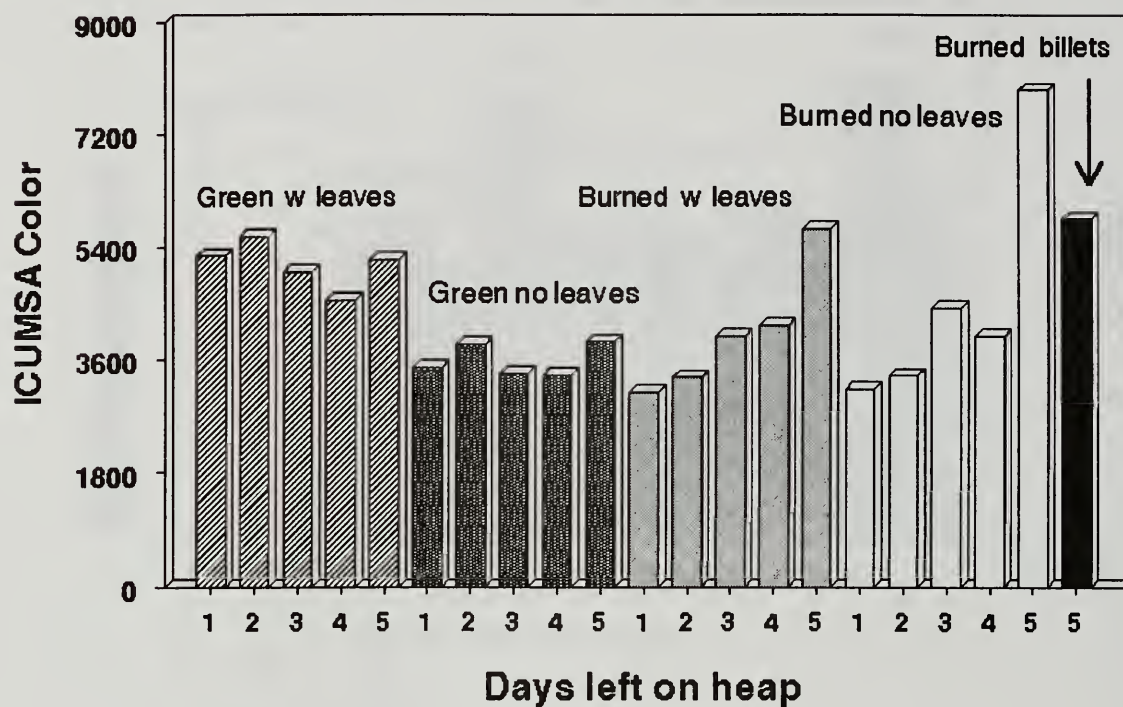
**Figure 8. Deterioration Study
Ash in Soldier-Harvested Cane**



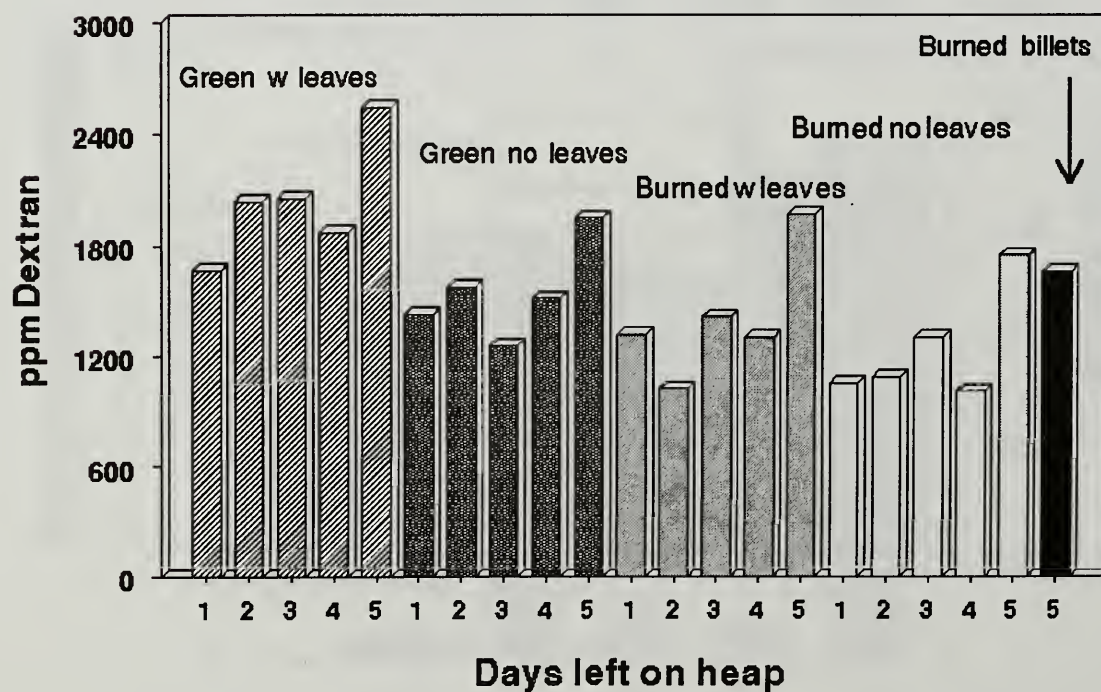
**Figure 9. Deterioration Study
Color in Soldier-Harvested Cane**



**Figure 10. Deterioration Study
Total Polys in Soldier-Harvested Cane**



**Figure 11. Deterioration Study
Dextran in Soldier-Harvested Cane**



FRACTAL STRUCTURES FOR UNIFORM FLUID DISTRIBUTION IN THE SUGAR INDUSTRY

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INTRODUCTION

In most cases better fluid distribution benefits the performance of any chemical heat- or mass transfer unit operation. However, for some applications, the benefits are not as pronounced as for others. For example, fluid distribution is crucial for packed distillation towers and not as important for tray distillation towers [1].

Although the problem of fluid maldistribution is frequently addressed in the chemical and petrochemical industry or general chemical engineering publications [2,3], the sugar industry literature remains almost free of references on this important subject. Nevertheless, significant economic benefits can be achieved by optimizing conventional fluid distributors or designing new equipment utilizing the advantages of improved distribution systems. A clear understanding of shortcomings of the existing distributors will help elucidate the benefits provided by more efficient fluid distribution systems.

Existing and potential applications in the sugar industry

A review of unit operations currently utilized by the sugar industry indicates that processes involving liquid flow through a column filled with granulated material are among the most sensitive to fluid distribution. Efficiency of these unit operations is dependent on the uniformity of the concentration front of dissolved components. Any deviation from "plug" flow reduces performance separation efficiency of a column. Following are the processes used in the beet industry, cane sugar mills and refineries, for which fluid distribution is of crucial importance.

Industrial chromatography for syrup or molasses desugarization

Juice and water softening

Carbon or ion exchange decolorization columns

For some other processes the effect of fluid distribution is less obvious, but the optimization may result in significant savings. Use of fractal structures for air distribution in sugar conditioning silos may serve as a good example of such application [4]. A similar concept has been applied for turbulence reduction in a pilot clarifier design.

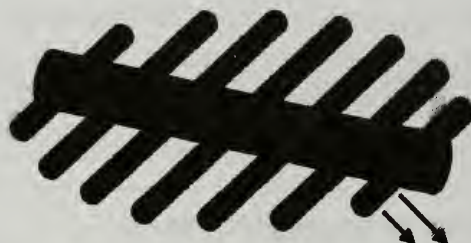
Once the importance of fluid distribution is understood and the damage from maldistribution evaluated, the corrective action should be taken. Existing fluid distributors can be modified or new equipment can be designed providing improved fluid distribution. Amalgamated Research Inc. (ARi) is currently exploring both alternatives.

Disadvantages of conventional distributors.

Most common distributors used in chromatographic, softener, and decolorization applications are quite simple in design. When these processes were transferred from pilot to industrial scale the fluid distribution issue was obviously overlooked. The major drawback of common types of distributors is rooted in the lack of symmetry, which makes a scale-up task very complicated.

An example of a conventional lateral pipe distributor is shown in Figure 1. Typically the centrally located inlet is connected to a series of interconnected pipes with outlet holes. The residence time from the inlet to each hole varies depending on the distance from the inlet. For the same reason the pressure drop is different for each path from an inlet pipe to an outlet hole. Since the concentration of dissolved components changes continuously, different residence time leads to spreading or "smearing" of the concentration front and therefore to loss of separation efficiency.

Figure 1
An Example of a Conventional Distributor



Conventional practice of distributor design based on high pressure drop or variable outlet hole size leads to another set of problems. Among them is dependence of distribution quality on the feed rate. This problem is sometimes addressed as a turndown ratio. The ability of a distributor to convert fluid from a feed pipe into a uniform two-dimensional surface inside the column is extremely important for many industrial applications. For example, in simulated moving bed (SMB) chromatography recirculation flow varies significantly during an operation cycle. Obviously, variable distribution quality in each step results in reduction of overall process efficiency.

Distributors based on fractal geometry

A new generation of fluid distributors based on fractal geometry has been described extensively in the recent literature [5,6]. This innovative idea has resulted in a number of patents (issued and pending) on fluid distributors and engineered fractal cascades [7,8]. Fractal distributors originally installed in large-scale chromatographic columns (up to 7 meters in diameter), have been

modified for ion-exchange and decolorization applications, air distribution in conditioning silos, gas-liquid systems, etc.[9]. A sample illustration of a fluid distributor for industrial chromatographic columns is shown in Figure 2. Seemingly complicated, the distributors are rather easy to install. The original distributors have been in industrial operation for more that seven years. The cost compares favorably with conventional designs.

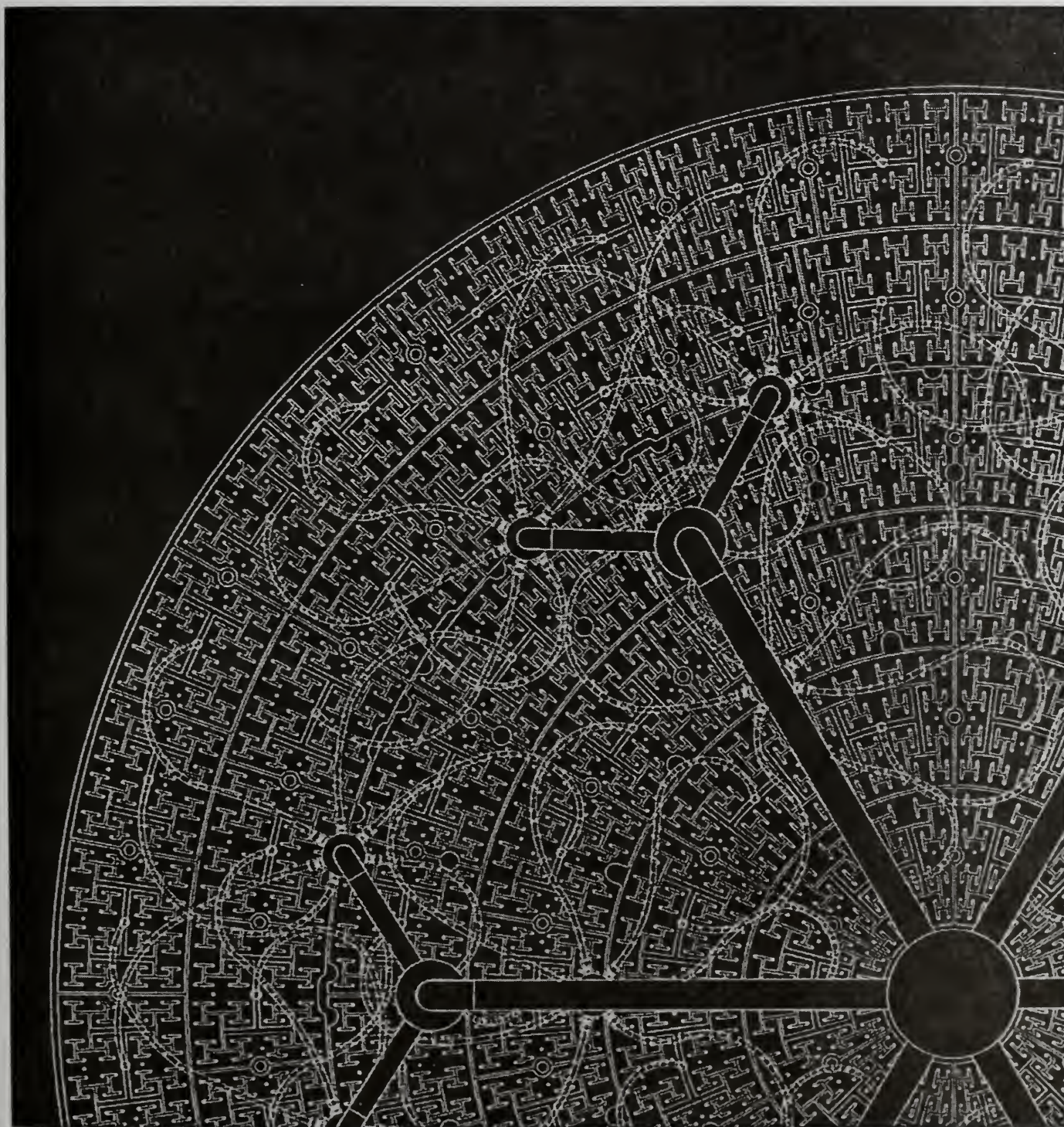


Figure 2. Fractal distributor for industrial chromatographic columns.

EXPERIMENTAL DATA

To confirm the quality of fluid distribution for gas-liquid systems (absorption and distillation applications) a 1.5 meter prototype fractal has been manufactured and tested at the Laboratory of Process Equipment of Delft University in the Netherlands. The fractal distribution network has remained unchanged and the open area was provided to allow the counterflow of gas. A prototype with more than 50% open area is shown in Figure 3. The quality of distribution was evaluated by physical measurement of flow out of each exit hole of a distributor. The results plotted in Figures 4 and 5 show the distribution of fluid at various liquid loads and density of exit holes. The surface of the distributor was divided into three areas (O-outer ring, M-middle ring and I-inner ring). The data have demonstrated superior distribution with the exception of the central portion of the distributor designated I1 through I6. At low liquid load the distributor was not completely full, therefore the distribution was partially distorted. We have found that the problem was caused by air entrapment in the pre-distributor manifold. After the problem was corrected the distribution improved drastically which is illustrated by Figure 6.

The test demonstrated high efficiency of fractal structures for uniform distribution across the column cross-sectional area. Results from fractal gas-liquid distributors have been confirmed by an alternative tracer injection test method. A pulse of food grade blue dye was injected in the chromatographic column and the samples were collected downstream at the exit. The response curve characterized the distribution quality in the column. It was shown that the distribution quality in a 4 meter-diameter column was equivalent to distribution in a 7.5 cm diameter pilot column. It may be impossible to achieve such a result without using a self-similar fractal structure. The experiments are described in more detail in our previous publications [10].

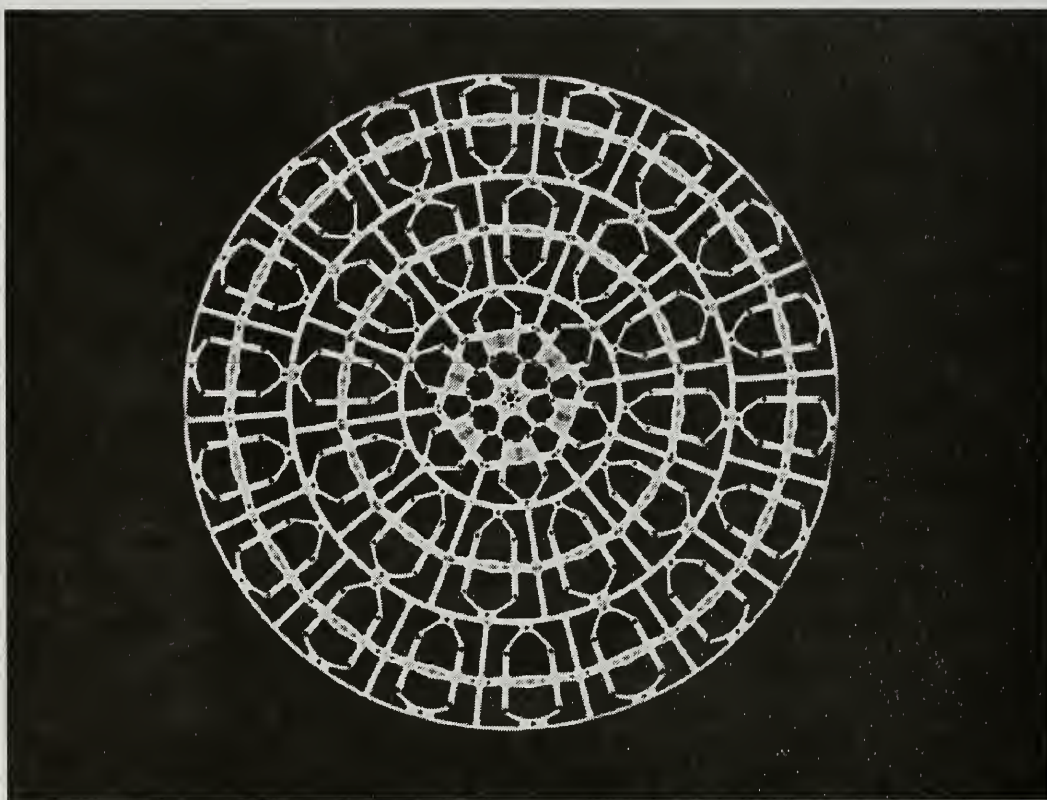


Figure 3. Fractals for gas/liquid applications

Figure 4. Distribution at Various Liquid Loads (high density - 576 exit holes).

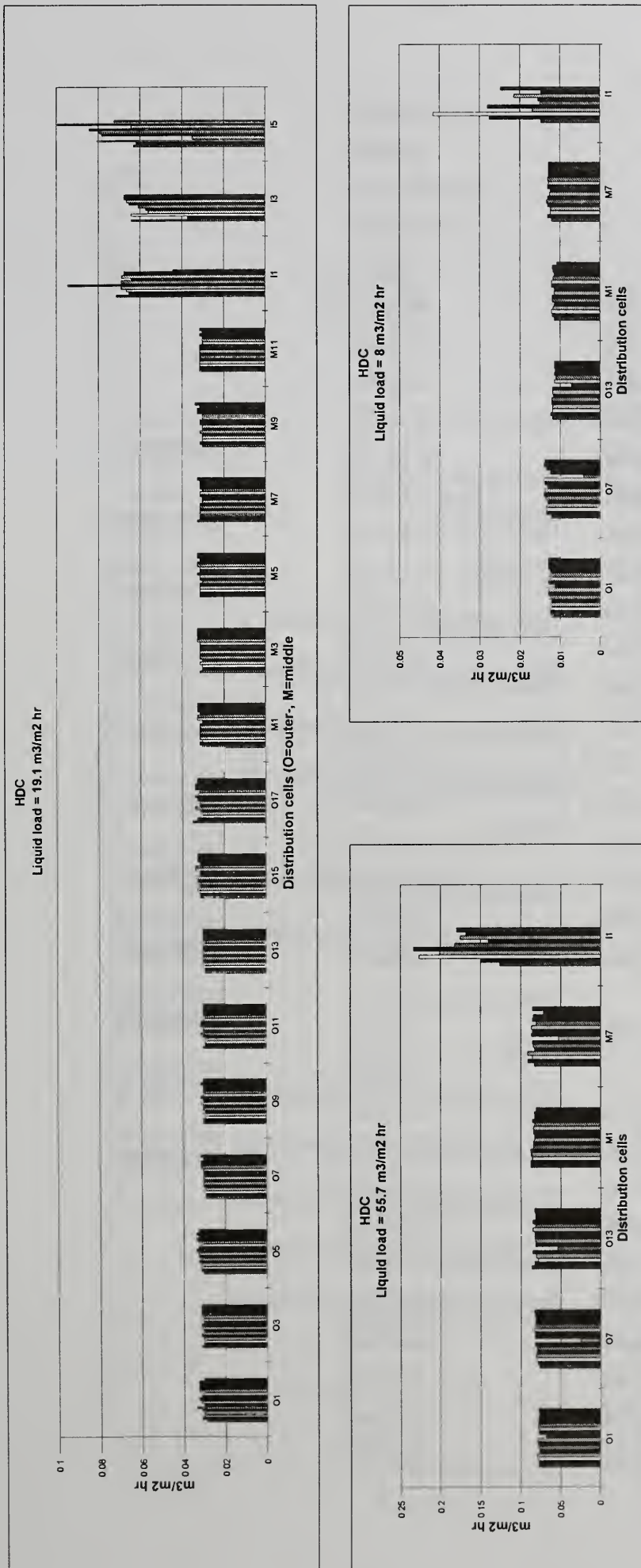


Figure 5. Distribution at Various Liquid Loads (low density - 144 exit holes)

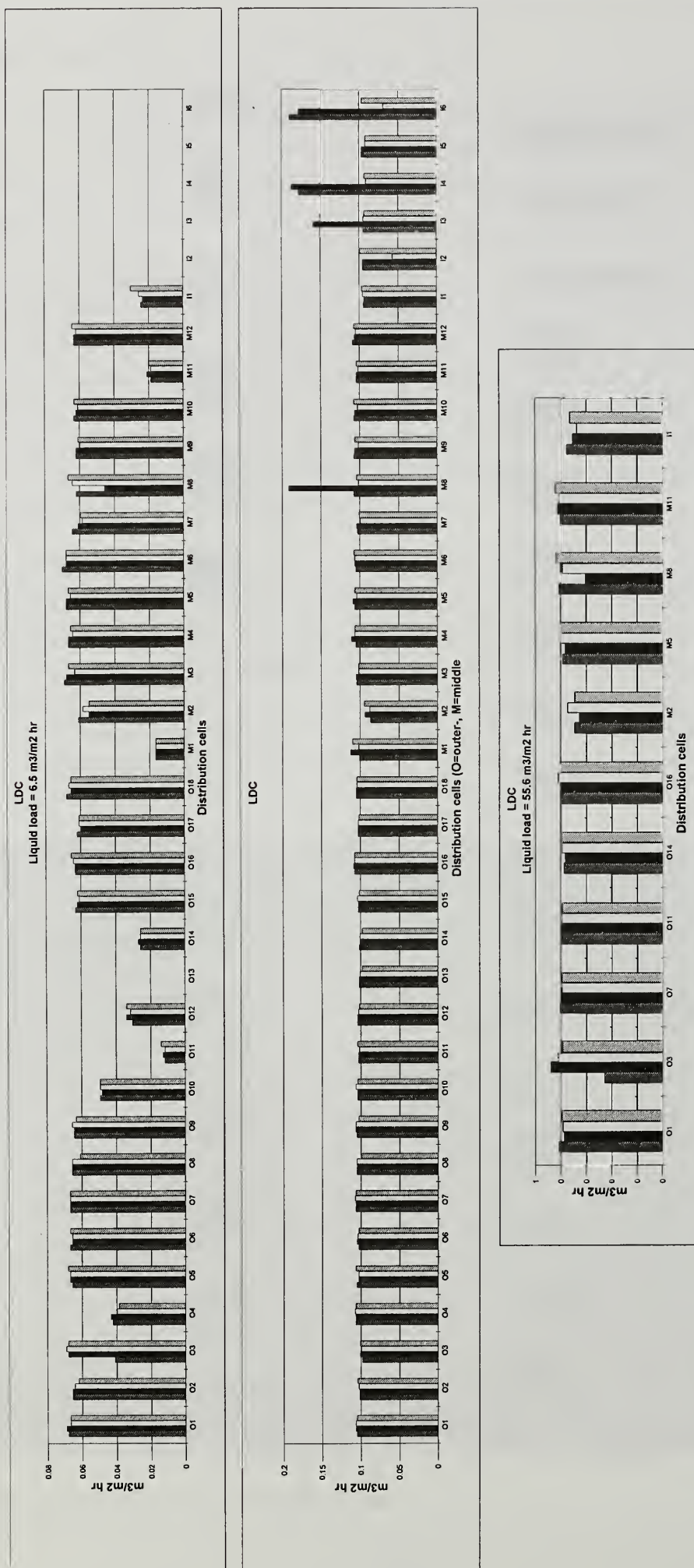
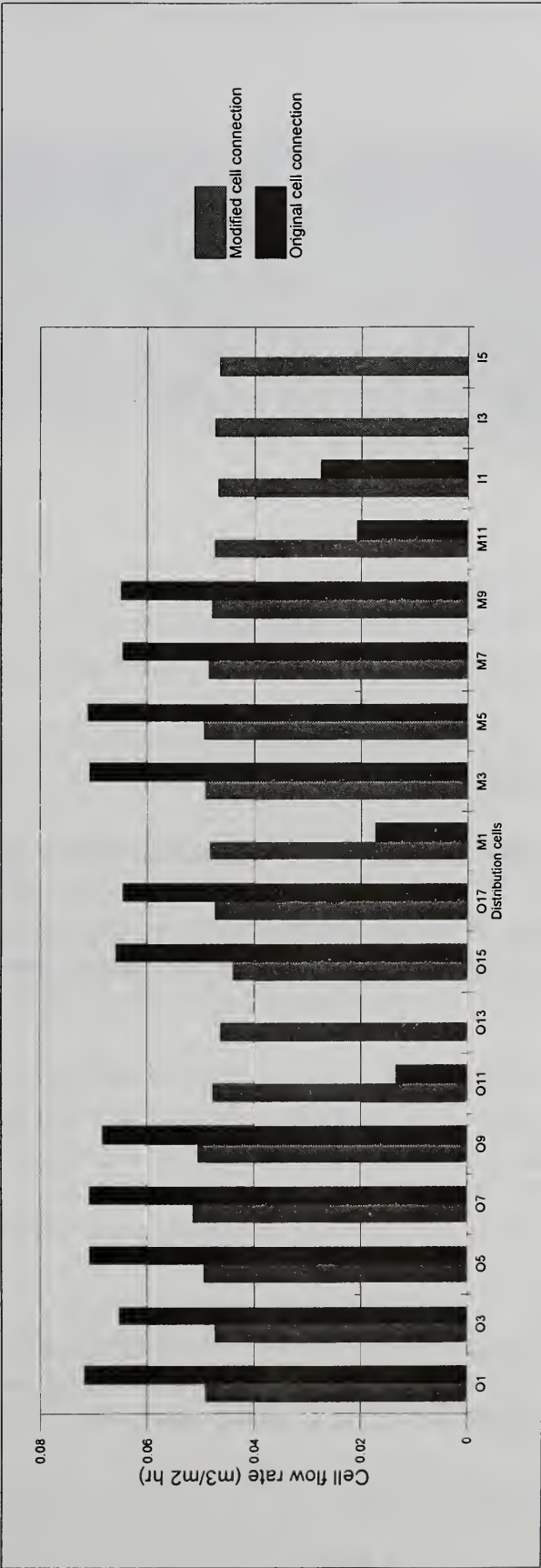


Figure 6. Improved Performance after Modification of pre-distributor Manifold.



Another example of superior quality fractal distribution is demonstrated in Figure 7. An interface between water and 15 Brix sugar solution above the resin bed remained undisturbed at flowrates of 500 bed volumes per hour.



Figure 7

Interface between Water and 15 Brix Juice above the Resin Bed during Sweet-off Cycle

General benefits of fractal distributors

A few features of fractal fluid distributors will remain the same regardless of the application.

1. The self-similarity of fractals automatically implies easy scale-up from any size pilot installation. The manufacturing techniques may vary depending on the scale but the distribution quality does not change.
2. The uniformity of fluid distribution provided by fractals cannot be matched by using any conventional distributor. Each of the multiple pathways in a fractal distributor is hydraulically equivalent to all others. This guarantees superior fluid uniformity across the column.
3. Hydraulic equivalence also provides extremely wide turndown ratio without any loss of distribution accuracy.
4. As opposed to conventional distributors where uniformity is achieved by high pressure drop, fractals are very low pressure drop devices. Significant energy savings and reduced equipment cost may be realized through the use of fractal structures.

Specific benefits for various applications

The general features of fractal distributors bring out some benefits specific to certain applications. Some of the examples listed below illustrate the benefits of fractals mainly for applications where liquid flows through a granular bed, such as ion-exchange, decolorization, etc.

1. Because of better quality of fluid distribution, the concentration front will move through a resin bed uniformly. By-passes and stagnant zones will be essentially eliminated resulting in an overall increase of column efficiency. More complete utilization of resin or carbon exchange capacity can be achieved.

2. During the regeneration cycle a similar phenomenon can be observed leading to reduction of regenerant use, and more efficient regeneration. Water use (and hence evaporation load) can be reduced significantly during sweet-off cycles.

3. In unit operations with relatively fast kinetics, such as softening, higher overall throughput can be achieved by using short bed depth. This can only be accomplished with superb distribution quality. In conventional applications fluid maldistribution is usually compensated for with excessive bed depth, which in turn limits the column throughput.

CONCLUSIONS

– The sugar industry utilizes several unit operations that are very sensitive to efficiency of fluid distribution. A few examples include, but are not limited to chromatography, ion exchange and decolorization processes.

– Lack of uniform fluid distribution in existing systems results in low overall performance, high energy use and other associated costs.

– Fractal fluid distributors provide almost ideal fluid scaling and overcome the disadvantages of existing devices and open the opportunity for a new generation of industrial equipment.

– Since fractal distributors have been proven efficient in many industrial operations, the search for new applications and evaluation of the benefits should continue.

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STUDY OF SUCROSE SOLUBILITY AND CRYSTALLIZATION RATE USING NMR TECHNIQUES

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Abstract

This study has examined sucrose solubility from an unconventional perspective by determining the sucrose solubility under normal vacuum pan boiling conditions, and hence, under non-equilibrium conditions. Sugar boiling trials were conducted in a pilot batch vacuum pan, in which the massecuite crystal content was monitored continuously using modified low resolution NMR instrumentation. Crystal content readings were used in conjunction with mass balance data to determine the changes in sucrose solubility in relation to changes in molasses purity and impurity/water ratio. In addition, high resolution solid state NMR techniques have been employed to examine the microscopic interactions between sucrose, water and impurities.

INTRODUCTION

Sucrose solubility in molasses is indelibly linked to the study of molasses exhaustion, despite the fundamental differences between these two properties. Molasses exhaustion is the point where no appreciable quantities of sucrose can be economically recovered, whereas sucrose solubility relates to the equilibrium endpoint at which no further sucrose will crystallize. This study has embarked on a course to study the phenomenon of sucrose solubility under normal sugar boiling conditions in a pilot vacuum pan. This approach is based upon two main experimental criteria: the ability to continuously measure crystal content (CC) in the vacuum pan, and knowledge of the mass balance state of the vessel.

High resolution solid state NMR techniques have also been used to probe the effects of water and impurities on sucrose mobility in syrups and molasses through the determination of transverse relaxation (T2) time constants of hydrogen nuclei within the sucrose molecule. This work will serve as a reference point for further studies of synthetic syrups with known impurity compositions.

MATERIALS AND METHODS

Crystallization trials were conducted in a 15 L capacity pilot vacuum pan. In each case, a pure syrup footing was concentrated to 80-83° brix before seeding with a sucrose slurry in butyl alcohol. The massecuite footing was allowed to equilibrate before feeding with factory liquor or molasses. Following each period of feed and evaporation, the vacuum pan was switched to recycle (no net evaporation) and allowed to equilibrate over a period of 15 minutes, or until the CC stabilised to a steady level. The CC reading was then used in conjunction with mass balance data to calculate the sucrose saturation coefficient.

Instrumentation consisted of a Bruker NMS 120 Minispec low resolution (20 MHz) NMR spectrometer, which had been modified to fit a glass flow-through cell in the spectrometer probe (Bruker dual 18RTAS). CC data was measured using a two-point ratio technique (van Putte, 1995), which is based on the ability to discriminate between the solid and liquid contributions to the NMR decay signal. The acquisition program was written in the Exp spel NMR programming language, supplied by Bruker. Massecuite was drawn continuously from the base of the vacuum pan by a peristaltic pump and passed through the horizontal flow-through cell of the spectrometer magnet before returning to the pan. Massecuite flow rate was approximately 1.5 kg/min.

Proton T2 measurements of sucrose in syrups and molasses were determined using a Bruker Avance 400 DPX NMR spectrometer, fitted with a solid state probe with magic angle capability. T2 values were determined using the CPMG method.

RESULTS AND DISCUSSION

Solubility Trials

Each solubility trial produced a record of CC for the duration of the strike. Figure 1 provides an example, with significant events throughout the trial summarized in Table 1. Mass balance data and CC readings were then combined to determine the sucrose saturation coefficient at particular times during the strike.

To date, trials of factory liquors and molasses has been restricted to higher purity material. Consequently, investigation has been limited to impurity/water ratios of less than one. Figure 2 illustrates data derived from crystallization trials using liquor or A molasses as feed. To date, although results have shown rough agreement with literature data (van der Poel *et. al.*, 1998), the cumulative errors which occur in the mass balance of the crystallization vessel prevent the identification of genuine solubility trends over a narrow range of I/W ratio.

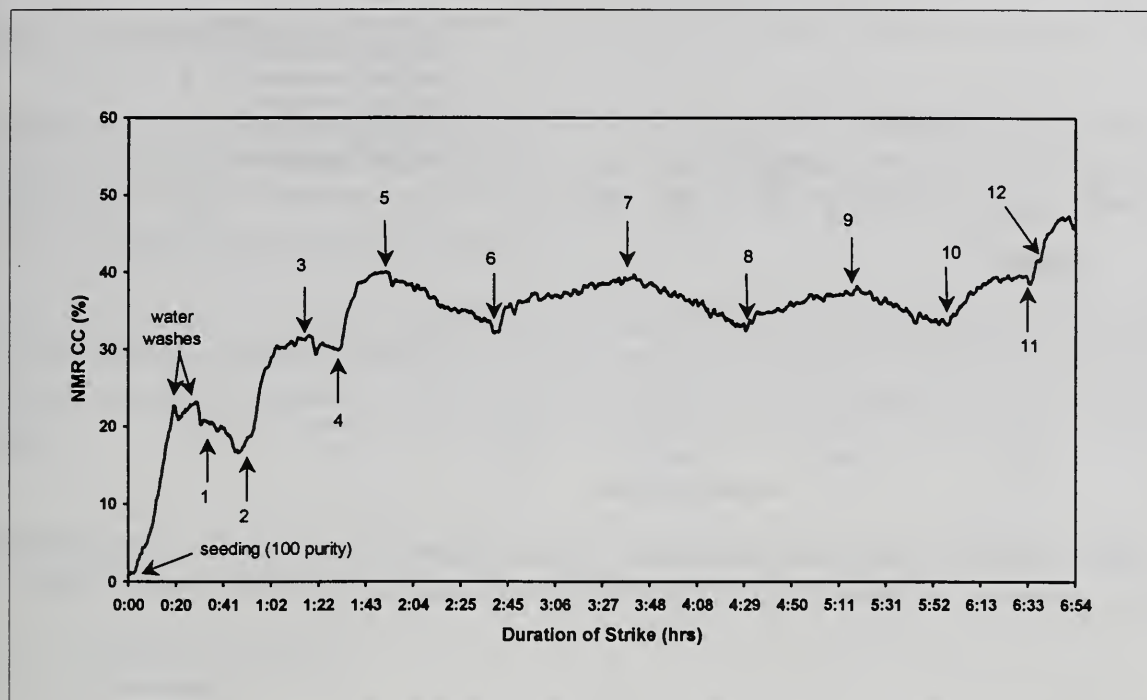


Figure 1. Record of massecuite CC measurement for a B massecuite strike in SRI pilot vacuum pan. Significant events during the strike are numbered and are explained in Table 1.

Table 1. Key of events during crystallization strike illustrated in Figure 1.

Chart Region	Comments	Evaporation (/g)	A Molasses Feed (/g)
1-2	Feed and evap.	272	548
2-3	Recycle	0	0
3-4	Feed and evap.	149	400
4-5	Recycle	0	0
5-6	Feed and evap.	114	1337
6-7	Recycle	0	0
7-8	Feed and evap.	114	1721
8-9	Recycle	0	0
9-10	Feed and evap.	191	1362
10-11	Recycle	0	0
11-12	Evaporation only	190	0
12-	Recycle	0	0

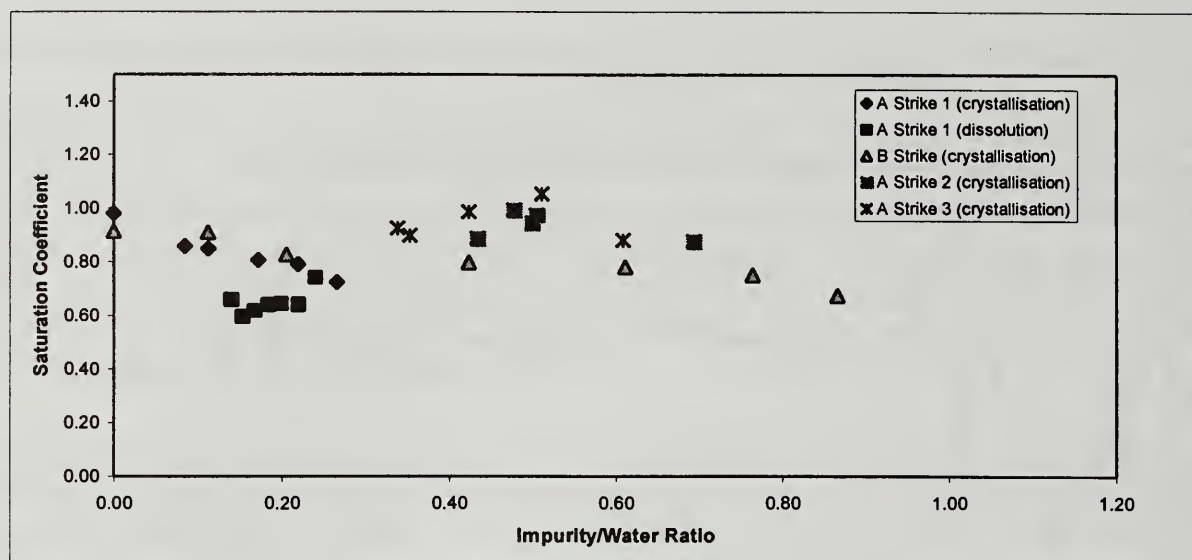


Figure 2. Plot of sucrose saturation coefficient versus impurity/water ratio for experimental boils of factory liquor and molasses, as determined by mass balance and crystal content data.

Crystal Content Monitor

A notable benefit to arise from this work has been the development of the on-line CC monitor. The device is able to measure CC in massecuite from seeding of the initial footing until final discharge of the massecuite from the vessel. With an operating range of 0-50% and a precision of 0.2% units of crystal content, the instrument has the potential to provide a new control regime for vacuum pan operation. This instrument will undergo factory trials in the future to examine the feasibility of such an application. An example of an A massecuite strike is illustrated in Figure 3.

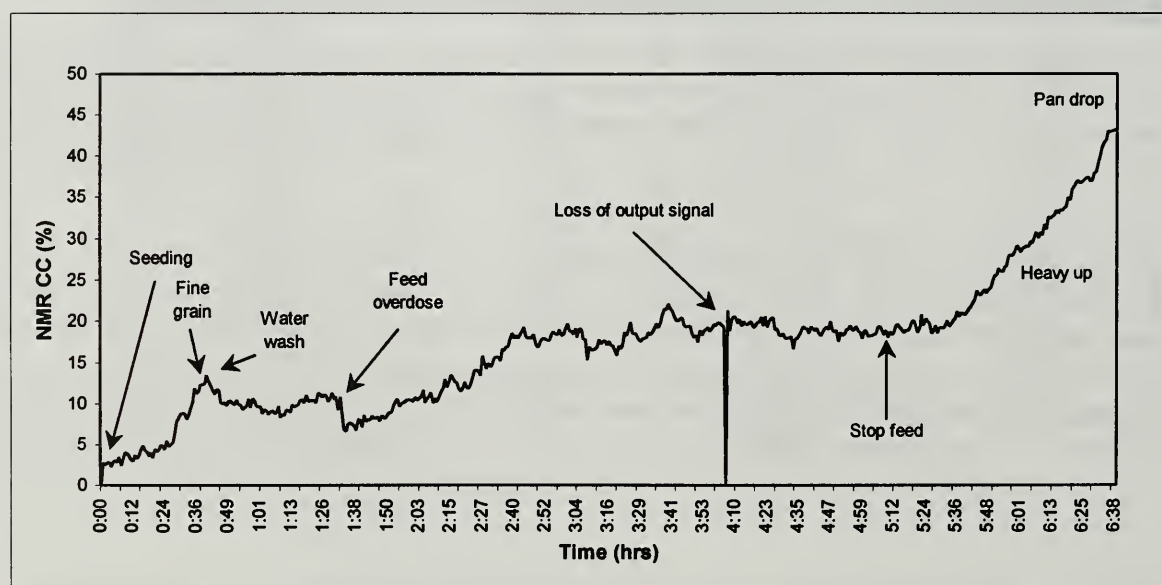


Figure 3. Record of massecuite CC measurement for normal A massecuite strike in SRI pilot vacuum pan. Anomalies in pan control revealed by trends in CC.

High Resolution NMR Studies

Preliminary studies have been undertaken to examine the effects of purity and moisture on sucrose mobility in syrups and molasses. In particular, transverse relaxation time constants (T_2) were determined for sucrose protons in factory liquor, and A and B molasses. Figure 4 illustrates the T_2 times for the sucrose G1 proton.

The result shows a strong dependence of T_2 , and hence sucrose mobility on purity, although further work is required to differentiate this trend from viscosity effects. Future studies will not only examine the behavior of T_2 values with purity and moisture levels, but also with purity types.

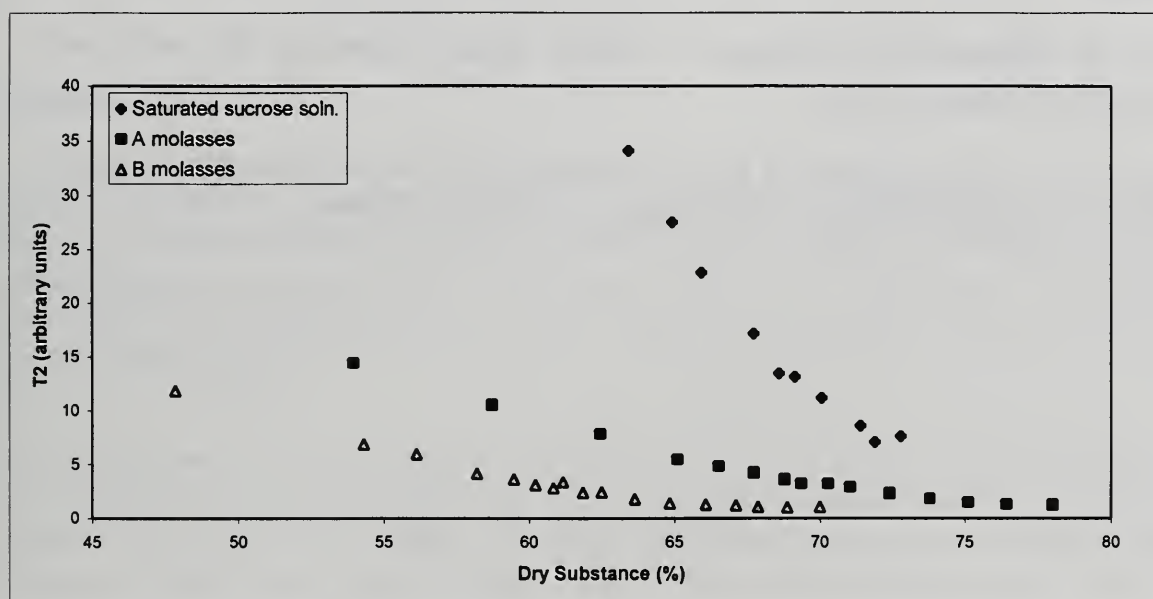


Figure 4. Plot of NMR T_2 relaxation rate constant of sucrose G1 proton with changing water content and purity.

CONCLUSIONS

This study has examined sucrose solubility via an unconventional approach by determining the sucrose solubility under normal vacuum pan boiling conditions, and hence, under non-equilibrium conditions. Systematic errors in the mass balance required for calculation of the sucrose saturation coefficient has prevented a meaningful interpretation of results to date. However, it is anticipated that improvements to the pilot crystallization vessel in conjunction with the precision of the crystal content monitor will provide the means for further useful studies of sucrose solubility.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the technical assistance of SRI staff during the course of this study: Mr Stewart McKinnon, Mr Ken Miller, Mr John Williams, and Mrs Hilary Bartholomew. Helpful discussions with Dr Ross Broadfoot (SRI) and Dr Derek Pert (Bruker Australia) are also acknowledged. This work comprises part of the SRI project 'Investigation of Reduced Sucrose Solubility in Molasses' with financial support provided by the Sugar Research and Development Corporation (SRDC) and sugar mills.

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Filterability Study of Raw Sugar

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ABSTRACT

Filtration problems caused by impurities in raw sugar are well known in the refining industry. Among the filter-impeding impurities are starch, dextran, gums, waxes, protein, phosphates, other polysaccharides and other micro particulates which result in turbidity. Some authorities believe that the filtration impeding effects of these matters are primarily caused by their size rather than their chemical nature.

Filterability tests were performed at the SPRI laboratories, using a solution of various raw sugars at 55 brix, 70° C and CELITE 545 as a filtering aid. Filtration rate is defined as volume of solution collected in 35 minutes. Filtration rate was correlated to total polysaccharides, starch, dextran, turbidity, ash, color and pol. The results and conclusions are shown and the most significant correlations are discussed .

INTRODUCTION

The filterability of raw sugar decreases the capacity of the refineries. The experimental work described in this paper was carried out at the SPRI laboratories using raw sugar from many countries around the world. Also, a filtration equipment was used as shown in Figure 1.

PROCEDURES

Creation of Cake

- Assemble the pressure filtration unit mounting in a jacket.
- Start circulation of hot water to maintain 70° C through the jacket.
- Before assembling, make sure that the proper filter is in place.
- Make arrangements for air connection at 60 PSIG to be in place and safe.
- Place a glass measuring cylinder under the discharge valve.

- Arrange for an appropriate CELITE filter aid.
- Use CELITE in the form of a slurry, turn the air on and let the water drain out to build the cake.
- Disassemble the column to check the cake .
- Upper surface of the cake should be even (and in line with the top surface of the sieve cavity).

Filtration of Sucrose Solutions

- Prepare sucrose solutions of Brix 55
- When filtration is good, the cake is dry and porous. A slimy cake leads to a flow of filtration
- The higher the cake water content, the higher the cake resistance.
- The resulting filtration rate shown in Table 1 and also in Graph 1 is the volume collected in 35 minutes.
- The total volume of the tube was 120 ml.

RESULTS

For each sample, the analysis were made and are shown in Table 2.

Sugar with the same amount of impurities, from different regions around the world, can have different filterability.

The test showed that the higher the temperature of the solution is, the higher the filtration rate is. However, as the temperature goes up, the rate of sucrose inversion also accelerates. Filtration rate was correlated to total polysaccharides, starch, dextran, turbidity, ash color and pol. The results are shown in Graphs 2 to 8.

CONCLUSIONS

The effect of the suspended solids present in the raw sugar has been studied (2, 4, 5). The effects of these particles are primarily caused by their size rather than by their chemical nature. Some of the impurities that are inside the raw sugar crystal are also responsible for difficult filtration.

The correlation data appear to suggest that a combination of impurities, rather than one in particular, causes filtration problems. The strongest correlations are with turbidity (0.93), total polysaccharide (0.83) and color (0.75).

ACKNOWLEDGMENTS

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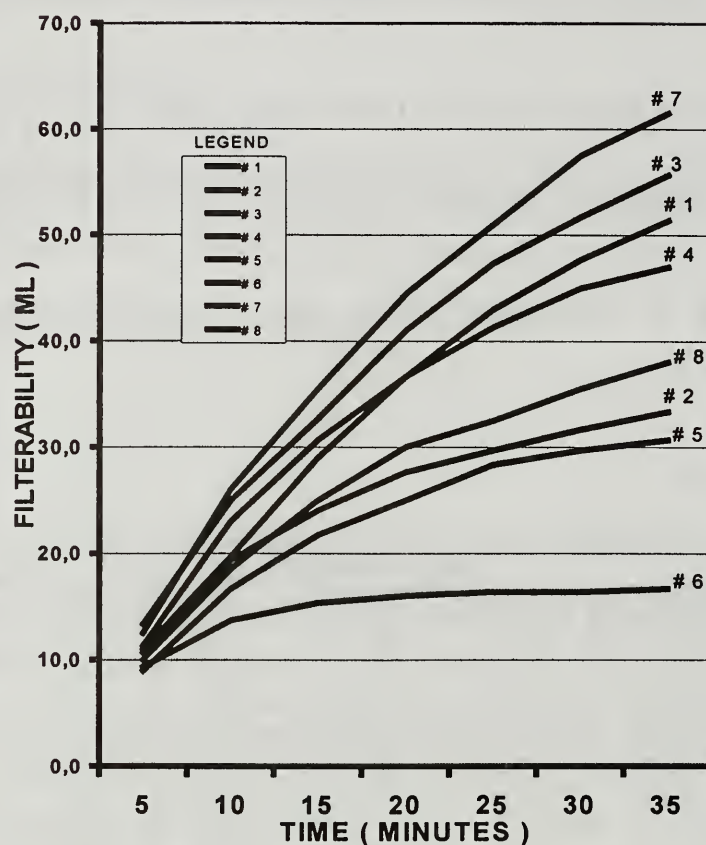
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Table 1 – Filtration Rate (ml)

RAW SUGAR	TIME (minutes)						
	5	10	15	20	25	30	35
SAMPLE # 1	11.3	23.0	30.7	36.7	43.0	47.7	51.3
SAMPLE # 2	10.7	19.3	24.0	27.7	29.7	31.7	33.3
SAMPLE # 3	13.3	25.0	32.7	41.0	47.3	51.7	55.7
SAMPLE # 4	11.0	19.7	29.0	36.7	41.3	45.0	47.0
SAMPLE # 5	9.0	16.7	21.7	25.0	28.3	29.7	30.7
SAMPLE # 6	9.3	13.7	15.3	16.0	16.3	16.3	16.7
SAMPLE # 7	12.5	26.0	35.5	44.5	51.0	57.5	61.5
SAMPLE # 8	10.0	18.5	25.0	30.0	32.5	35.5	38.0

FILTERABILITY OF RAW SUGAR

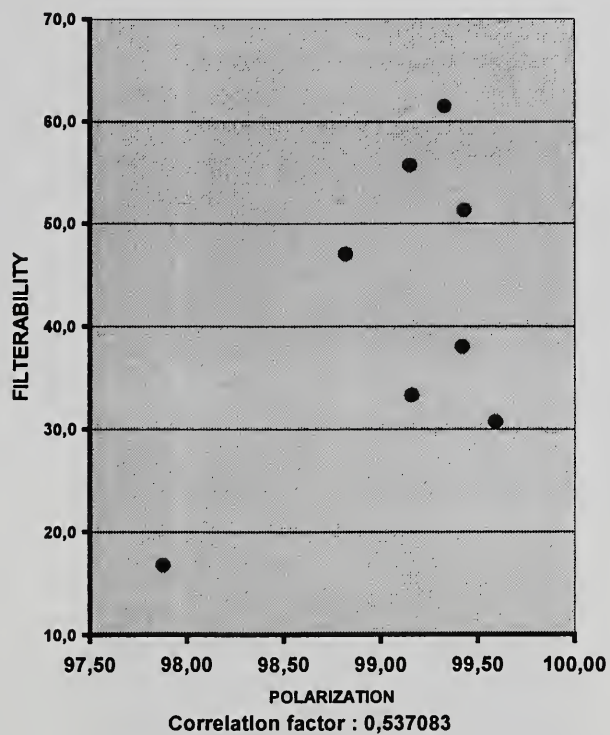


Graph 1

Table 2 – Sugar Analysis

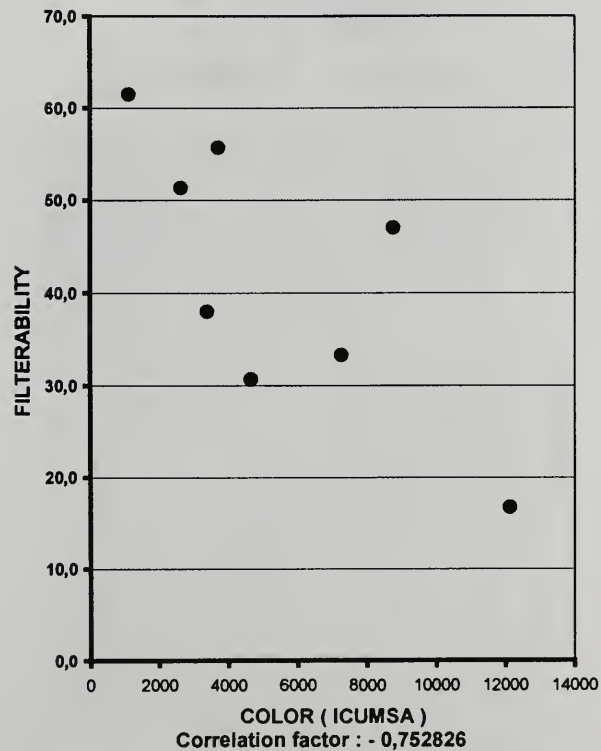
SAMPLES	Filterability (ml/35 min)	Polarization (%)	Color (ICUMSA)	Turbidity	Ash (%)	Starch (ppm)	Dextran (ppm)	Total Poly (ppm)
SAMPLE # 1	51.3	99.43	2634	1251	0.324	279	410	951
SAMPLE # 2	33.3	99.16	7287	2072	0.533	410	611	1558
SAMPLE # 3	55.7	99.15	3716	881	0.371	117	434	773
SAMPLE # 4	47.0	98.82	8767	829	0.190	281	444	1519
SAMPLE # 5	30.7	99.59	4662	2054	0.350	258	494	1186
SAMPLE # 6	16.7	97.88	12124	2989	0.518	117	885	1795
SAMPLE # 7	61.5	99.33	1122	508	0.146	243	423	770
SAMPLE # 8	38.0	99.42	3393	1099	0.190	147	825	1136

POL vs. FILTERABILITY



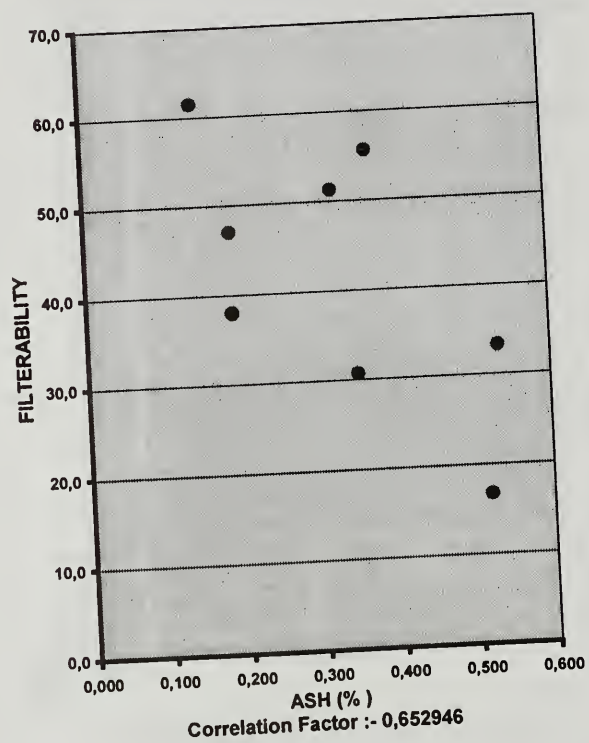
Graph 2

COLOR vs. FILTERABILITY



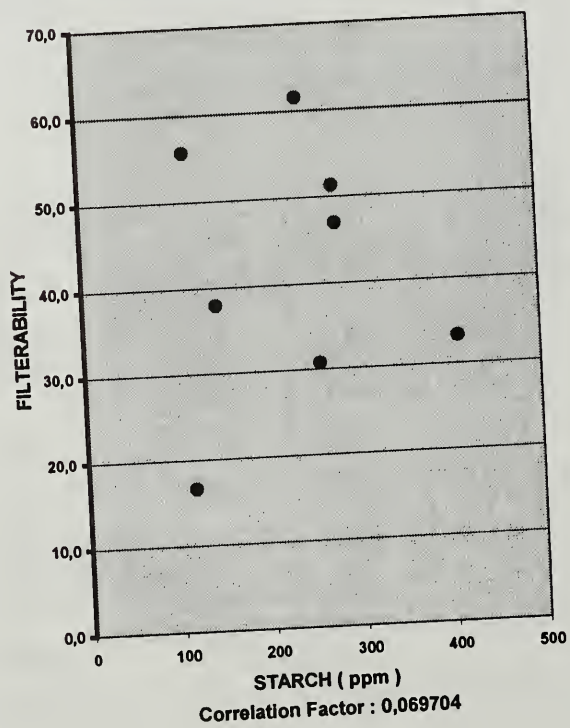
Graph 3

ASH vs. FILTERABILITY

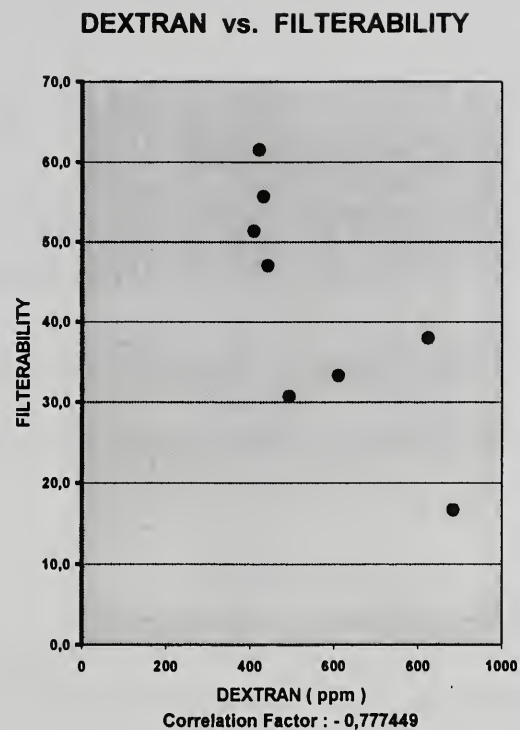


Graph 4

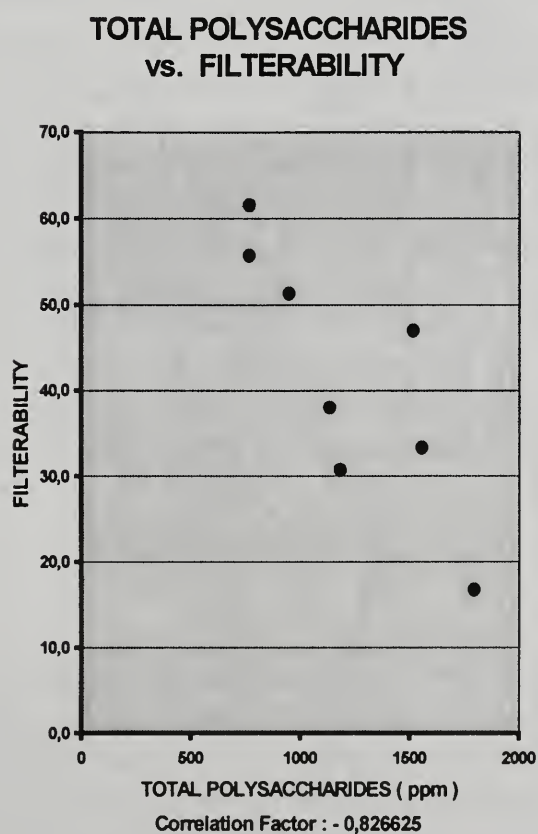
STARCH vs. FILTERABILITY



Graph 5

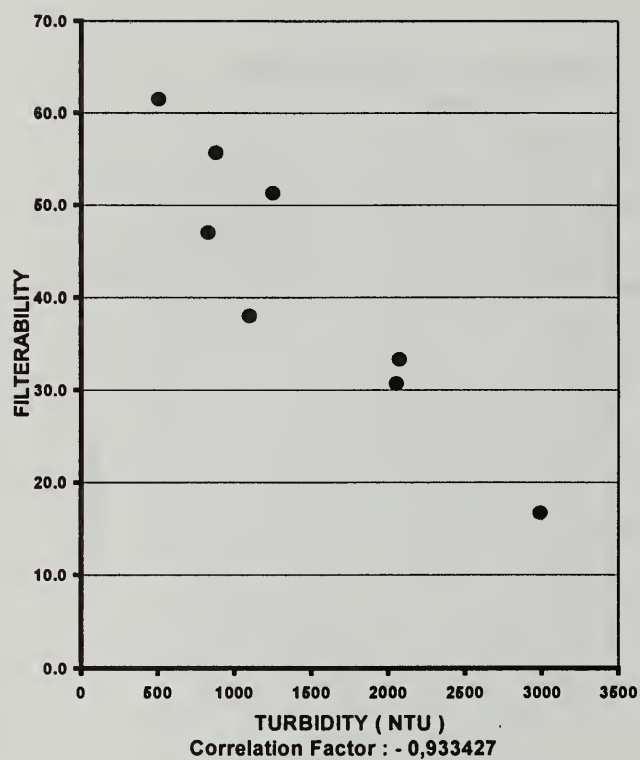


Graph 6



Graph 7

TURBIDITY vs. FILTERABILITY



Graph 8

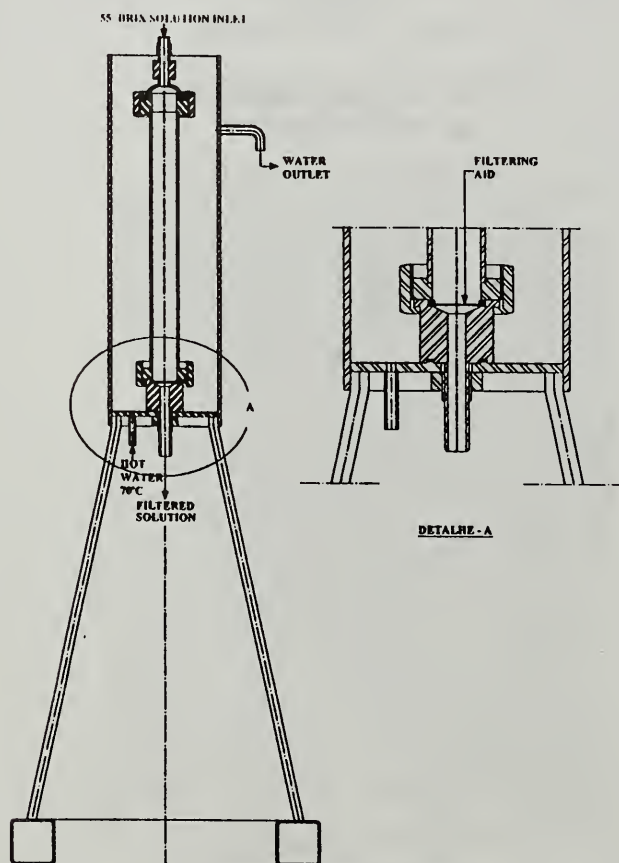


Figure 1. The filtration apparatus.

THE NON SUCROSE PROFILE IN TWO LOUISIANA CANE SUGAR MILLS

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ABSTRACT

The objective of sugar processing is to recover the maximum amount of sucrose from the cane entering the mills. The complex nature of cane juice is affected not only by the individual processing steps but also by the time of harvest. The effect is reflected by different values of several parameters. Specific effects of individual processes can reveal where sucrose is at greater risk of degradation, which affects the quality and yield of sugar. Samples from one Louisiana sugar mill were evaluated during the 1999 harvest for pH, brix, purity, color, turbidity, invert, polysaccharide, cations and ash. Samples included mixed juice, clarified juice, syrup, A, B, and C sugars and A, B, and final molasses during the early, mid and late season. A similar set of samples was obtained from a second mill during the latter part of the season. The study of process stream parameters revealed patterns of change at different stages of the grinding season. In mixed juice, pH was fairly acidic, with normal values ranging from 5 to 6. Invert declined across the season, with a moderate increase late in the season. The other parameters, including color, turbidity, polysaccharide, cations, and ash showed a mixed pattern of changes. Color increased, as expected, from juice to syrup. Conductivity ash decreased unexpectedly from juice to syrup. Turbidity decreased in clarified juice but increased in syrup. Total polysaccharide decreased in clarified juice and also in syrup. The main objective of this study was to establish a database which could serve as a reference about the nature of process streams in Louisiana and for troubleshooting problems.

INTRODUCTION

The aim of the sugar manufacturing process, which starts with extraction of cane juice and ends with crystalline raw sugar, is the isolation of a high quality final product without significant loss of sugar. Sugar manufacturing is a series of unit operations. It is crucial to observe the performance of each operation, as it is the basis for the next operation. Each unit operation causes specific changes in the composition of the material being processed. Without knowledge of changes taking place in unit processes, one cannot control the overall process.

Cane juice is a complex mixture whose composition depends upon a variety of factors, including the geographical location of the crop, the cane variety, cultural practices and the time in the season of the harvest. (1,7). Cane is exposed to changing weather conditions from harvest to crush throughout the grinding season, which may cause a variety of changes in the juice, reflected by the composition of the juice. Sometime a slight variation, if not accounted for, could lead to greater loss of sugar and also cause other difficulties in operation. In order to achieve a balanced but efficient operation, it is necessary to gather information about the non-sucrose components of process streams at different stages of the grinding season.

In this study, we gathered information about parameters that are not normally analyzed in the core lab due to their complexity, expense and difficulty. These tests generally analyze for minor constituents in the cane juice, such as polysaccharides, invert and ash, along with color, which impact the process and final quality of the raw sugar produced.

MATERIALS AND METHODS

Samples of mixed juice, clarified juice, syrup, A, B, and C sugars and A, B, and C (final) molasses were composited over 8 hours of processing during corresponding weeks from one Louisiana sugar factory. The samples were frozen immediately on dry ice for transportation to the SPRI Laboratories. Analyses included Brix, pH, invert, color, turbidity, total polysaccharides, cations (as Ca + Mg), and conductivity ash.

For study purposes, the campaign was divided into three phases: Early season, mid season; and late season. The early season samples (comprised of samples PS 1, 2, 3) were collected during late September and early October. The mid-season samples (comprised of samples PS 4, 5, 6) were collected during late October and November. The late season samples (comprised of samples PS 7, 8, 9) were collected during late November and December.

Late in the season, there arose the opportunity to also evaluate the process stream samples from another Louisiana sugar factory.

Invert was measured by HPLC; calcium and magnesium were measured by ion chromatography; conductivity ash was measured by the ICUMSA method; total polysaccharides was determined using the SPRI method; color was determined using the ICUMSA method except that sodium hydroxide was used to adjust pH instead of TEA buffer; turbidity was measured by a difference method using the color method and is reported as ICU.

RESULTS & DISCUSSION

Analytical results for process stream samples from Mill 1 are shown in Tables 1 through 9. Results of analysis of samples from Mill 2 are shown in Table 10.

Brix (RDS).

Brix of the mixed juice was in the range of 13.5 to 16.3 (Table 1), except for the lowest value of 12.6, which indicated some operational adjustments in the factory. Otherwise the brix showed an upward trend from early to mid season, which is expected at the beginning of the season, as the cane is less mature. This is in agreement with results reported in the Cane Sugar Handbook, 12th Ed. However, the decline in brix during late season, can be explained due to an operational situation as the mill house was not properly functional. Brix of syrup is a good indicator of evaporator performance. The brix of the syrup in this study was in the range of 45 to 61, on the lower side of the average value for this size of sugar mill. It was an indication of some operational problems encountered at the evaporator station. Brix of molasses depends upon the level of purities required for A and B sugars. As higher purity sugar is desired, more water will be used at the centrifugal, thus the brix of the molasses will be on the lower side, as demonstrated at this factory.

Purity.

Sucrose comprises about 13% of the raw juice and 70-90% of the soluble materials. (2) Industry-wide the percent sucrose on solids value is referred to as the purity of the juice or syrup. After brix, purity is of utmost importance to a sugar processor as these values are used mainly for determining the mass flow of dry substances and sugar entering the factory and accounting for it as it leaves the factory as sugar, molasses, bagasse, and as a loss during the process. In this study the values were slightly higher than the factory reports.

The purity rise from mixed juice to clarified juice was from 1.2 to 2.7 degrees on most sampling days (Table 2). The purity of A and B molasses showed a rise in the early season, then started falling slowly from mid season to late season. These figures are important for designing a good pan boiling scheme. A and B sugars pols were above 99 in most cases. Clarke (1985) discussed the trend of making high pol raw sugar. Purity is a good indicator of the efficiency of each processing step by conventional means.

Invert.

Although glucose and fructose, the constituents of invert, are sugars, for the purposes of the cane sugar mill, they are considered non-sugars, that is, not sucrose. Invert is an indication of sucrose loss to hydrolysis, it is a source for color formation, and it can slow crystallization rate.

Mixed juice had quite high values of invert in the early part of season (Table 3), but it trended downward as the season proceeded. It exceeded 10% on solids during early season, but during the late season it decreased to about 4% on solids. Clarified juice had lower values of invert than the raw, showing the destruction of invert during liming (with a corresponding increase in the color of clarified juice). The invert in clarified juice during the early season was over 5% on solids, but it dropped to 2% on solids during mid and late season. The level of invert in syrup was almost the same as clarified juice with exceptions during mid season, when there was an increase. The values of invert in raw sugar were in the range of 0.02 to 0.16 % on solids for A and 0.02 to 0.59 % on solids for B sugars, indicating good process control. With the exception of the first sampling

period when invert was very high in C sugar, average invert values in C sugar did not exceed 2% on solids the rest of the season. These figures are in general agreement with those reported in the literature (4).

pH.

pH is a major control parameter in sugar processing. A pH that is too low (below 5) can cause inversion and loss of sucrose and may also indicate microbial contamination. A pH that is too high (over 8.5) causes the destruction of reducing sugars, especially of the fructose, to organic acids and color.

The mixed juice in this study was on the acid side, ranging from 4.8 to 5.5, whereas the normal expected pH values would be between 5.3 to 5.8. There was a slight upward trend as the season progressed, reflecting, in part, the maturing of the cane. The pH of clarified juice was in the range of 6.5 to 7.2. The pH of syrup was unchanged throughout the season, ranging from 6.3 to 6.8, with an average value of 6.6 ± 0.15 , representing a pH drop of about 0.4 from clarified juice. This drop could represent the deposition of alkaline salts (Ca) on the evaporator tube walls in the form of scale. The same is true for pH of molasses being recycled at the pan floor. The pH of A and B molasses was over 6.5 most of the time, with the exception of weeks 5 and 6, when it was close to 6. This situation should be avoided since the molasses has to go through another boiling for recovery of sugar. The C sugar also had a pH slightly over 6 most of time.

Color.

Color constitutes a major component of non sucrose impurities to be removed in sugar processing. A discussion of the chemistry of colorants is beyond the scope of this study, but it is important to keep track of color throughout the process. It has been reported that only one third of the color in sugar streams comes from the cane plant, the rest is developed during processing. As explained by Gillet (5), during the cane sugar manufacturing process, both sucrose and non-sucrose impurities are subjected to heat, varying pH, air, iron (from equipment), added processing aids (such as lime) etc. Each of these factors has a distinctive effect on the development of color. The first stage of color formation in the sugar mill occurs in clarification. In clarifying the raw juice, heat and lime increase the color due to decomposition of the reducing sugars. In the evaporation and crystallization steps, color may be formed from caramelization and decomposition products due to overheating.

Mixed juice color did not change much during the season, averaging 9352 ICU over the season. The clarified juice averaged 9828 ICU, an increase of 5.1% over mixed juice, certainly within an acceptable range (Table 5). In sample PS 2, there was a 19.4% increase in color from mixed to clarified juice. In fact, there was an average 12% color increase from mixed to clarified juice in the first 6 sampling periods, but this was compensated by a decrease in color in clarified juice in the last 3 sampling periods.

Syrup increased in color over clarified juice on all but the last sampling date, averaging 11,280 ICU, representing a 14.8% increase over clarified juice color. On two sampling occasions in the mid-season (PS4 and PS6), the color increased by more than 30% (31.6% and 31.1%,

respectively). Large amounts of color formation during evaporation would indicate the necessity for better control.

The colors of A and B sugars were somewhat variable. A sugar color ranged from 617 to 1473 ICU, averaging 1002 for the season. This represents a 9% color transfer into the raw sugar from the syrup. The color of B sugar ranged from 1113 to 2673 ICU, averaging 1823 for the season. There was no obvious trend over the season.

Turbidity.

Turbidity represents insoluble material, colloidal material, suspended solids, gums, waxes and lipids. If this material is not removed from the process streams it will end up in the raw sugar, rendering it of poor quality. Also turbidity elements can cause problems with filtration.

Mixed juice turbidity averaged 128,639 ICU over the season, with large increases occurring late in the season. (Table 6). Clarification removed 96%, on average, of the turbidity. Clarified juice turbidity averaged 5197 ICU over the season. Turbidity increased in the syrup for all sampling periods, except PS6. The average syrup turbidity for the season was 7031, representing a 33.9% increase over clarified juice. As with color formation in the evaporators, the increase in turbidity in syrup is another area for concern and control. The turbidity may be a consequence of the color formation, with generation of insoluble color polymers, but may also represent small particles of scale and other deposits that form during evaporation.

Total Polysaccharides.

Polysaccharides present in juice and other process streams include starch, dextran and indigenous sugarcane polysaccharide (I.S.P.). These have a deleterious effect on processing, by increasing viscosity, polarization value and slowing crystallization rate. During crystal growth, the shape of sucrose crystals can be influenced by the presence of impurities. Dextran is preferentially adsorbed on the sucrose crystal face, causing that face to grow more slowly resulting in an elongated crystal.

In mixed juice (Table 7), polysaccharides averaged 6435 ppm for the season, ranging from 3880 to 8930 ppm. Polysaccharides tended to be higher in the early and late season. Clarification resulted in an average across-the-season polysaccharide level of 5066 ppm. This represents a removal of only 21.3% polysaccharides by clarification. As expected, there was little change in polysaccharides in syrup compared to clarified juice, averaging 4867 ppm in syrup, a decrease of 3.9%, which is within the variation of the method, as well as representing some small loss of polysaccharide to scale on the evaporator tubes.

Total polysaccharides in A sugar averaged 1156 ppm over the season, but there was a remarkable decrease in polysaccharide concentrations in the late season. Overall, crystallization into A sugar removed 76.2% of the total polysaccharide. However, the removal rate was 85.3% for the last three sampling periods, and 72.4% for the first six sampling periods.

Polysaccharides increased greatly starting with C sugar through to the final molasses, with values increasing steadily throughout the season in final molasses. In B molasses and final molasses, polysaccharides represent 1-2% of the solids.

Cations (Ca + Mg).

Ca + Mg in mixed juice were higher at the beginning and end of the season, averaging 2656 ppm in mixed juice over the entire season. There were no significant differences in Ca + Mg across mixed juice, clarified juice and syrup, with only a slight increase from mixed juice to clarified juice. These cations averaged 179 ppm in A sugar and 363 ppm in B sugar. These calcium levels would indicate good control over the clarification process.

Conductivity ash.

To estimate the recoverable sugars from juice or raw sugar, a simple relationship of pol and non-sugars contents is used industry wide. Among the non-sugars, some ash constituents have a high melassigenic coefficient. For more accurate determination of sucrose losses in final molasses, calculation is simplified by using conductivity ash.

The conductivity ash values of the mixed juice had a trend similar to the above cations – higher at the beginning and end of the season, with a slight decrease in mid-season. Season averages were 3.44% in mixed juice, 3.54% in clarified juice and 3.28% in syrup. The A sugar averaged 0.20% and B sugar 0.38% over the season.

A, B and final molasses all showed a fairly clear upward trend of ash across the season.

COMPARISON OF SAMPLES FROM TWO MILLS

There was an opportunity to evaluate the samples from another cane sugar mill in Louisiana during late season 1999. Most of the parameters demonstrated similar values in the factories, with a few exceptions (Table 10). Differences in brix are noted from syrup forward, with the brix being higher in Factory 2, due, as mentioned earlier, to operational limitations at Factory 1, causing their brix to be quite low. Invert in incoming mixed juice was lower in Factory 2 (3.10% vs 4.63%), and this is reflected in lower invert values throughout the process at each mill. Color values were very similar at both mills. Turbidity, total polysaccharides and Ca + Mg were significantly higher at Factory 2. For turbidity, from A sugar on, however, the differences disappeared. Ash tended to be slightly higher at Factory 1, but the differences were not significant.

CONCLUSIONS

The results of this study have shown the pattern of changes that occur in several important cane juice components throughout the cane sugar manufacturing process and throughout the season. The changes across the season were not very large. However, the trend in most parameters was to

be higher at the earliest and latest part of the season, with lower values during the mid season. The higher values at these times reflect quality issues with the incoming cane – in the early season the cane is immature, more leaves are coming in, and the factory is just getting “settled in.” In the late season, weather is beginning to deteriorate, there is rain and the cane is more recumbent, resulting in more trash and soil being brought into the factory. Color increased from raw juice to clarified juice and from clarified juice to syrup. Turbidity was about 95-96% removed during clarification, but it increased in syrup. There was also an increase in turbidity A sugar to B sugar.

In both of these factories, very high quality raw sugar (high pol, low color) was being produced, which results in a greater load of impurities and water going to molasses.

A benefit of this study is the establishment of a data base which can be used to determine expected levels of the minor components in processing. These components are not routinely tested, but can be the cause of process difficulties if they are too high or not controlled. The information in the data can be used to help troubleshoot problems. It is recognized that this is a small data set, and more data will be added in subsequent seasons.

ACKNOWLEDGMENTS

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Table 1: RDS (Brix) PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	13.0	14.6	12.7	13.0	16.0	10.3	15.2	13.5	12.6
Clarified Juice	13.8	13.8	14.0	14.0	15.0	14.0	13.3	13.5	12.8
Syrup	44.9	58.4	48.2	60.8	55.2	50.6	54.1	52.7	53.0
A Molasses	52.6	58.2	58.2	61.2	67.0	65.2	65.4	69.4	66.4
B Molasses	61.3	61.2	73.4	59.9	70.6	70.4	57.6	63.6	65.7
Final Molasses	85.3	78.4	83.6	82.8	81.2	81.8	80.4	83.0	79.4

Table 2: PURITY PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	78.5	76.6	84.2	78.5	84.8	84.5	88.5	89.9	85.9
Clarified Juice	78.9	78.5	85.6	86.0	87.5	88.1	89.7	88.4	88.8
Syrup	84.2	84.6	86.6	86.4	88.5	89.1	88.2	87.4	88.0
A Sugar	99.5	99.6	99.6	99.6	99.6	99.6	99.2	99.4	99.7
B Sugar	99.5	99.5	96.6	98.5	99.5	99.2	98.7	98.4	98.9
C Sugar	96.6	90.1	94.5	94.5	93.6	91.7	90.5	92.3	87.3
A Molasses	66.8	67.8	69.2	76.4	66.3	65.4	65.8	62.4	68.8
B Molasses	53.5	52.0	54.5	61.4	53.4	52.7	49.5	49.0	46.2

Table 3: INVERT (% solids) PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	10.30	13.90	9.61	9.50	8.63	2.53	1.91	4.63	4.35
Clarified Juice	6.30	5.56	5.00	4.00	2.00	2.36	2.41	3.04	2.41
Syrup	5.82	5.39	5.23	8.91	4.35	2.06	3.36	3.44	3.60
A Sugar	0.50	0.12	0.02	0.04	0.02	0.02	0.02	0.14	0.16
B Sugar	0.41	0.54	0.48	0.04	0.02	0.59	0.02	0.40	0.24
C Sugar	6.00	1.38	1.70	1.05	1.44	1.19	2.32	1.80	1.28
A Molasses	15.06	15.17	12.46	7.22	10.25	8.00	8.35	8.24	8.27
B Molasses	20.92	18.48	17.97	11.27	14.93	13.99	11.23	12.11	11.42
Final Molasses	22.96	17.15	24.42	29.66	12.0	14.24	12.16	12.86	11.56

Table 4: pH PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	4.9	4.8	5.0	5.0	5.1	5.5	5.3	5.4	5.1
Clarified Juice	7.2	7.0	7.2	7.2	6.7	6.5	7.2	7.0	6.9
Syrup	6.3	6.7	6.8	6.7	6.5	6.7	6.7	6.6	6.6
A Sugar	6.4	6.4	6.4	6.5	6.4	6.6	6.6	6.7	6.4
B Sugar	6.5	6.6	6.5	6.8	6.6	6.7	6.8	6.8	6.7
C Sugar	6.3	6.1	6.1	5.8	6.2	6.1	6.3	6.4	6.3
A Molasses	6.8	6.5	6.5	7.0	6.2	6.7	6.7	6.8	6.9
B Molasses	6.6	6.4	6.2	6.7	6.1	6.7	6.6	6.8	6.8
Final Molasses	6.3	5.9	5.6	6.1	5.8	6.0	6.1	6.3	6.3

Table 5: COLOR (ICU) PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	9000	9,667	9,000	9,000	8,500	9,000	10,333	9,333	10,333
Clarified Juice	9,974	11,544	10,090	10,000	9,132	10,003	9,020	9,260	9,426
Syrup	11,844	12,183	11,660	13,157	9,142	13,112	10,882	10,536	9,000
A Sugar	1,557	958	808	1,473	1,010	782	1,100	715	617
B Sugar	1,113	1,701	1,678	2,663	2,673	1,857	1,324	1,712	1,682
C Sugar	14,207	14,595	7,908	11,851	9,746	11,835	12,320	14,365	16,056
A Molasses	29,794	34,396	29,751	40,707	40,949	33,038	34,032	40,333	37,200
B Molasses	44,555	45,331	44,819	46,833	58,773	42,167	54,208	53,333	56,000
Final Molasses	71,469	70,333	91,500	87,750	113,000	94,400	85,500	120,667	99,000

Table 6: TURBIDITY (ICU) PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	120,000	119,666	126,600	112,000	116,000	118,000	87,815	177,000	180,667
Clarified Juice	3,518	6,077	3,913	4,000	5,396	5,384	6,233	5,425	6,831
Syrup	5,819	9,617	7,171	11,169	6,701	2,738	6,552	7,015	6,500
A Sugar	618	584	561	1,073	558	480	334	488	400
B Sugar	525	1,118	656	1,627	2,207	1,196	789	978	1,119
C Sugar	8,402	8,194	3,603	5,226	6,598	8,113	7,336	6,508	8,315
A Molasses	13,407	14,276	18,576	26,292	36,454	28,602	27,844	29,334	25,214
B Molasses	21,197	23,663	26,966	32,000	41,798	37,500	38,231	44,334	49,667
Final Molasses	29,672	28,000	41,167	46,750	69,667	52,800	39,500	63,000	52,000

Table 7: TOTAL POLYSACCHARIDES (ppm on solids) PROFILE ACROSS PROCESS STREAMS

Sample/week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	7,500	6,101	3,880	6,500	7,202	8,930	6,102	4,113	7,585
Clarified Juice	4,128	6,536	5,683	5,500	5,254	5,094	4,644	4,179	4,577
Syrup	3,358	5,989	4,835	7,389	4,470	4,763	4,127	4,471	4,400
A Sugar	1,040	1,448	2,068	1,750	1,163	1,020	493	831	590
B Sugar	1,034	1,783	1,816	2,022	1,720	1,428	725	914	805
C SUGAR	5,815	4,393	3,564	4,805	2,947	4,234	3,392	3,369	3,093
A Molasses	12,425	8,358	13,167	11,525	11,101	10,350	10,252	10,813	9,826
B Molasses	13,107	16,424	16,788	14,875	15,815	16,181	14,990	14,508	15,900
Final Molasses	20,617	22,991	21,005	27,835	23,341	25,197	21,065	21,029	20,295

Table 8: Ca+Mg (ppm on solids) PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	2700	2,800	2,600	2,000	1,519	2,166	3,782	3,246	3,089
Clarified Juice	2,200	2,700	2,250	2,600	2,914	2,365	3,315	2,903	3,343
Syrup	2,400	1,900	2,960	4,430	3,105	2,176	3,566	3,394	3,400
A Sugar	174	138	119	288	143	155	208	150	240
B Sugar	162	326	231	451	526	394	390	343	442
C Sugar	3,332	2,983	1,286	1,712	2,077	1,994	2,589	2,482	3,080
A Molasses	6,833	6,554	6,962	10,146	8,756	4,807	10,273	9,718	10,782
B Molasses	9,824	11,046	9,970	11,384	13,356	6,638	14,270	14,210	15,962
Final Molasses	13,517	14,200	13,401	16,894	18,085	19,401	24,211	18,380	21,446

Table 9: CONDUCTIVITY ASH PROFILE ACROSS PROCESS STREAMS

Sample/Week	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	PS 7	PS 8	PS 9
Mixed Juice	3.50	3.47	3.67	3.4	3.33	3.04	3.38	3.73	3.45
Clarified Juice	3.64	3.55	3.49	3.52	3.58	3.17	3.41	3.67	3.81
Syrup	3.45	3.58	3.17	3.32	3.11	3.32	3.16	3.23	3.15
A Sugar	0.34	0.15	0.16	0.26	0.21	0.16	0.21	0.13	0.20
B Sugar	0.24	0.35	0.25	0.45	0.63	0.42	0.32	0.37	0.37
C Sugar	2.42	2.43	0.99	1.28	1.80	1.82	2.00	1.97	3.04
A Molasses	6.78	7.27	6.20	6.37	7.79	7.50	8.44	7.53	7.84
B Molasses	6.98	8.76	8.45	8.50	10.83	10.08	11.80	11.05	11.06
Final Molasses	10.97	11.87	11.87	11.08	13.42	13.03	13.34	13.19	15.55

Table 10: COMPARISON OF NON-SUCROSE ACROSS PROCESS STREAMS FROM TWO SUGAR MILLS DURING LATE GRINDING SEASON 1999

Sample		Brix	Purity	Invert	pH	Color	Turbidity	T.Polys	Ca+Mg	Ash
Mixed Juice	F1	13.5	86.6	4.63	5.4	9,333	17,700	4,113	3,246	3.45
	F2	14.3	84.1	3.10	5.3	9,500	52,250	7,253	4,308	3.22
Clar. Juice	F1	13.5	88.4	3.04	7.0	9,260	5,425	4,179	2,903	3.81
	F2	13.4	88.9	2.54	6.9	10,513	6,838	5,895	3,126	3.22
Syrup	F1	52.7	87.4	3.06	6.6	10,536	7,015	4,471	3,394	3.15
	F2	64.7	88.7	2.98	6.8	11,100	9,307	5,594	1,233	2.98
A Sugar	F1		99.4	0.14	6.7	715	488	831	150	0.20
	F2		99.5	0.12	6.8	770	500	928	158	0.17
A Molasses	F1	69.4	62.4	8.24	6.8	40,333	29,334	10,871	9,718	7.84
	F2	72.5	72.3	7.63	7.0	29,387	23,252	11,595	4,231	7.16
B Molasses	F1	63.6	49.0	12.11	6.8	53,333	44,334	19,508	1,421	10.6
	F2	77.5	55.6	11.47	7.0	49,500	41,500	18,895	6,680	10.7
Final Mol.asses	F1	83.0		12.86	6.3	63,000	63,000	21,029	18,380	15.55
	F2	79.7		12.28	6.3	60,250	60,250	25,951	9,587	13.88

Note: F1 represents Sugar Mill1, and F2 represents Sugar Mill 2. Samples from Sugar Mill 2 were collected during the late season only.

R & D ON PAPER-MAKING FROM BAGASSE IN GUITANG

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Guangxi Guitang (Group) Co., Ltd. P. R. of China

ABSTRACT

This article describes the history, reality and prospects for research on paper-making from bagasse conducted by Guangxi Guitang (Group) Co., Ltd. in China and then focuses upon Guitang's paper-making technical features and the outlook of the on-going technology studies. Wet-storage of bagasse that substantially preserves the integrity and strength of bagasse fiber and pollution control measures dealing with black liquor, bleach waste water and white water are described. Despite some unfavorable pulp properties, such as shorter fiber length, more sturdy and brittle cellulose compared with wood pulp, cultural paper and household tissue that satisfy the Class A quality standards of China have been successfully made from bagasse stratified with a small portion of soft wood pulp and some necessary additive. Today paper products contribute an industrial value almost equivalent to that of sugar.

INTRODUCTION

The world market sugar price is currently running low, USD193.40 per metric ton for white sugar and USD 120.78 for raw. Due to the higher cane price in China compared to other countries, manufacturing costs cannot be cut down so much as the price that the sugar industry's profit margin is compressed. It is absolutely necessary to explore new way of comprehensive resource utilization to make better profits. In 1998 Guangxi Autonomous Region's cane yield was 31,000,000 t, yielding 32,000,000 t of sugar and 34,000,000 t of bone-dry bagasse. That means 13,000,000 t pulp or 14,000,000 t paper valued more than 7 billion RMB can be produced if the bagasse had all been used for paper making. In fact, pulp and paper making from bagasse is a profitable and practical solution for sugar mills undergoing such a difficult time.

China is deficient in forestry reserves, and its paper industry would have decayed if it had relied only on wood pulp. That is why a paper mill in China is so versatile and adaptable to all kinds of raw materials. Among all of the pulp and paper industries across the world, China marks the highest utilization ratio of vegetable fibers instead of lumber. It IS true in northern China for reed and wheat straw; however, in the south, almost all of the bagasse is burned for fuel by sugar mills, even in Guangxi--the best sugar cane comprehensive utilization area, no more than 35% of bagasse is used for other purpose. This is an amazing waste of a natural resource.

Paper Making History and Current Situation

Guitang became the first in China to make paper from bagasse, back in the early 1960s, exploring new ways to utilize sugar cane comprehensively. Along with decades of research and innovations, products we make from bagasse have been diversified from the initial relief printing paper and writing paper to two families: cultural paper and household tissue, with qualities that keep improving to a higher class. Paper mill capacity grew from 5000t in the early 1960s to 85,000t in 1999, among which 25,000 t are cultural paper made by Paper Mill I, 45,000 t are Class A cultural paper by Paper Mill II and 15,000 t by Tissue Plant. The brand-new Paper Mill II commenced operation in 1998. It has an advanced 45,000 t/a fine paper line adopting the world's latest technology of the 1990s. Another project of a 3,000 t/a tissue plant has been approved. Construction will start later this year and startup is expected in mid-2002. This plant will make premium household tissue from bagasse, bringing greater profit and compatibility.

Technical Features of Paper-Making

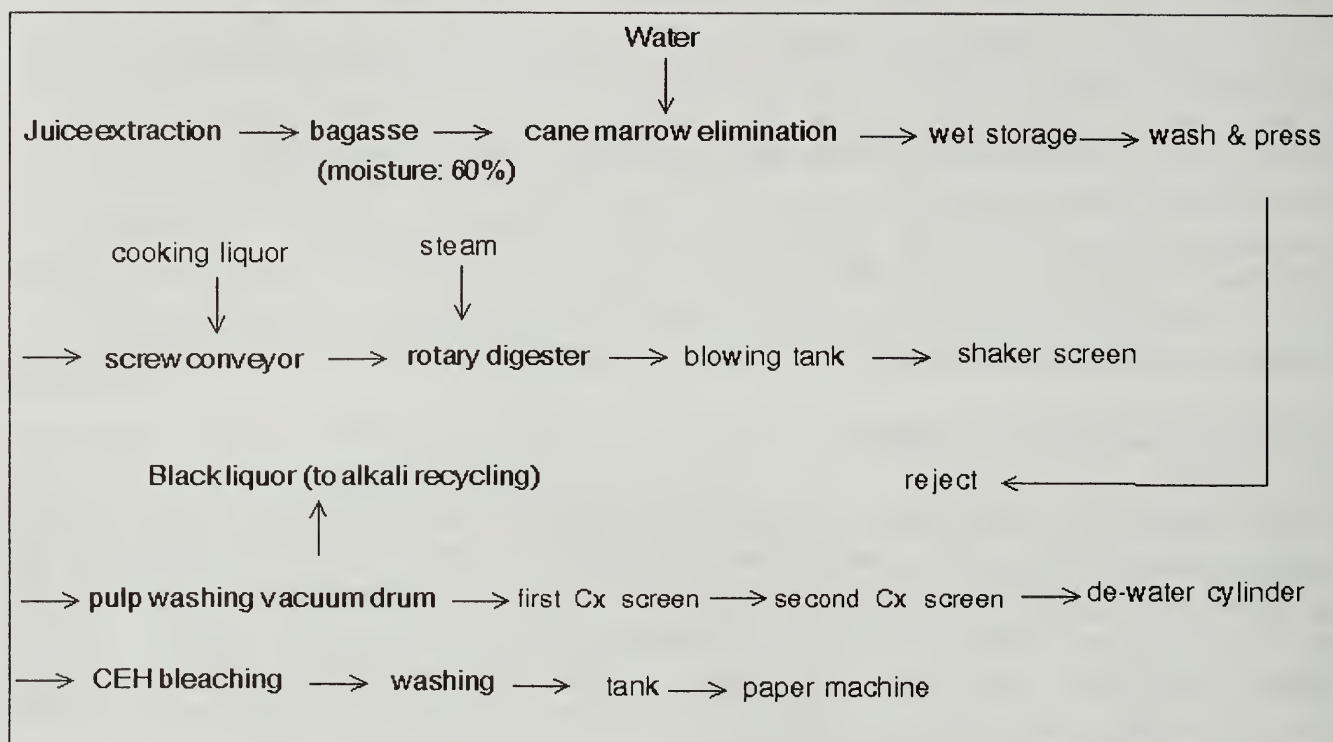
We have placed great importance on research and development of bagasse paper making technology since the later 1970s. Since the establishment of the Paper Institute in 1983, breaking progress has been achieved on process and pollution control for the bagasse paper industry. In 1984 "Pure Bagasse Tissue" and "Bagasse Bathroom Tissue for Export" were awarded the Excellent Technology Achievement of Guangxi; in 1992 "Bagasse Napkin" a major research subject of the State was granted a National New Product Certificate; in 1998 bagasse offset printing paper was supplied to the market.

Compared with softwood, bagasse fiber is shorter (0.8-1.2 mm) and wider (14-18 μm). Its length-width ratio is 60-80, wall thickness-lumen (empty space inside a cell) ratio is much less than 1. Bagasse pulp is characterized by average fiber length, thinner cell wall, fatter size, full of fine and fragile non-cellulose cells. In accordance with its fiber properties, it is likely to encounter drainage problem on wire, transfer trouble on press section and crepe difficulty on Yankee cylinder when making paper with bagasse pulp. We take special measures to deal with these occurrences.

1. Process flow and key techniques

A. Pulp Making

a. Flow sheet



b. Key techniques

1. Cane marrow elimination

Bagasse contains a large amount of fine cells and cane marrow (spongy non-fiber material in the center of cane stalk) that should be eliminated right after the bagasse comes out of the press mill; otherwise this will increase consumption of cooking liquor and lower the pulp and paper quality. Marrow in bagasse should be controlled below 20% after de-marrowing.

2. Wet storage

Dry storage and wet storage are two methods to preserve enough bagasse for the paper mills for year-round consumption. Dry storage is to compress the bagasse into cubes, stack the cubes and prevent them from water and keep ventilated. Dry-stored bagasse is vulnerable to deterioration and fire; it needs a large space and higher costs. Wet storage is to pave the bagasse on water-proof and acid-proof ground, showered with fresh water and clasp them by bulldozer layer by layer, up to 30 meters high, so as to extract oxygen and ferment the sucrose and other organic compounds inside. Density should be greater than 150 kg/m^3 , and moisture should always be kept above 70%. Wet storage protects the integrity and strength of bagasse fiber.

3. Washing & press

Bagasse should be piled up for at least 20 days when sucrose and other organic compounds degrade before it goes to the next procedure. Some of the fine cells, sand and waste should be washed out, which helps shorten the cooking time and improves cooking yield.

4. Cooking

When bagasse is blended with caustic digest liquor and saturated steam and cooked in a pressurized rotary digester, most of the lignin is removed before the temperature reaches 120°. So it is critical to control well the pressure/temperature curve and make sure the bagasse is simply well-done, no more, no less. Otherwise, a low cooking yield and poor fiber strength will occur.

Cooking ingredients:

Alkali: 15.5%

Sulfite: 17%

Cooking Liquor: 3.5-4%

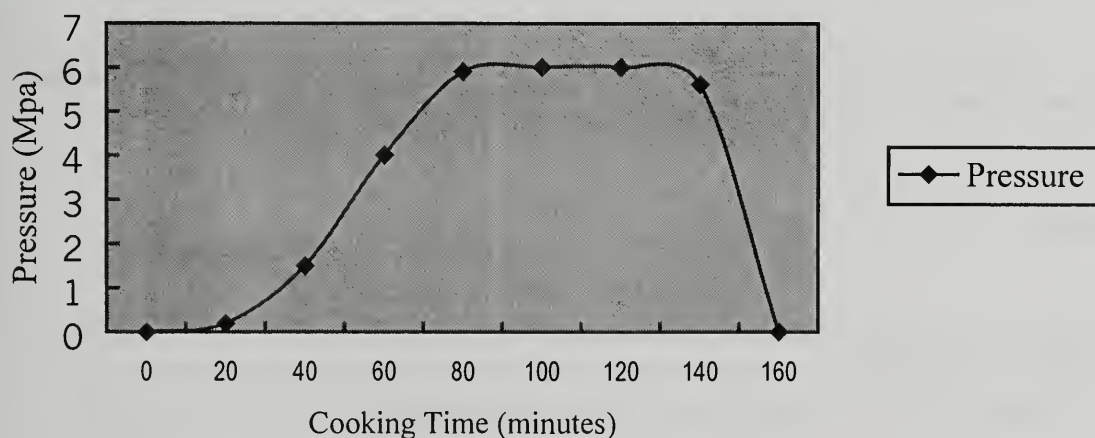
Pulp quality after cooking:

Residual Caustic: Not more than 8 g/l

Hardness: 9-15K

Shrives content: 8-17%

Pressure curve



5. CEH three stage bleaching

Process parameters:

Chlorination: Pulp consistency: 3.5%
 Processing temperature: Normal
 Duration: 35-40 minutes
 Pulp brightness after Chlorination: 40-50%
 Residual Chlorine: 0.02g/l

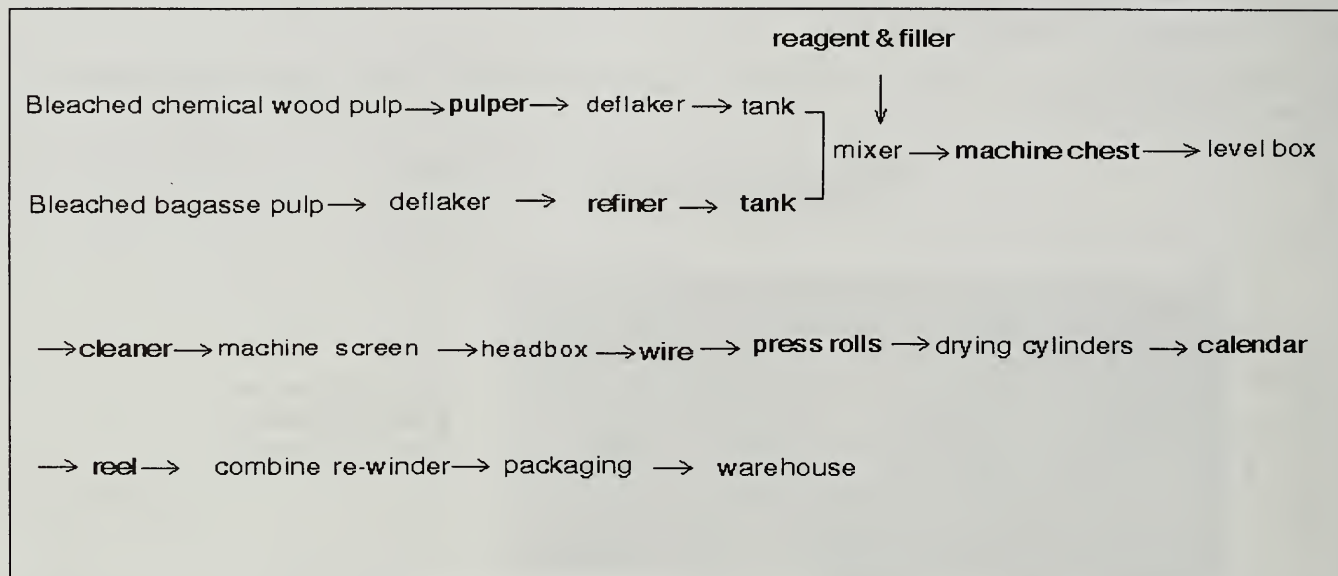
Alkali-Extraction: Pulp consistency: 8-10%
 Processing temperature: 60-70°C
 Duration: 90 minutes
 pH: 9-11

Hypochlorite bleach: Pulp consistency: 8-11%
 Bleaching liquor: 5%
 Temperature: 35-40°C
 Duration: 2 hours
 Pulp brightness after bleach: 78-82%
 Residual Chlorine: 0.02g/l
 Dirt: not more than 270mm²/500g

Over-bleaching should be avoided -- it will damage the bagasse fiber and weaken its strength.

B. Class A Cultural Paper

a. Flow sheet

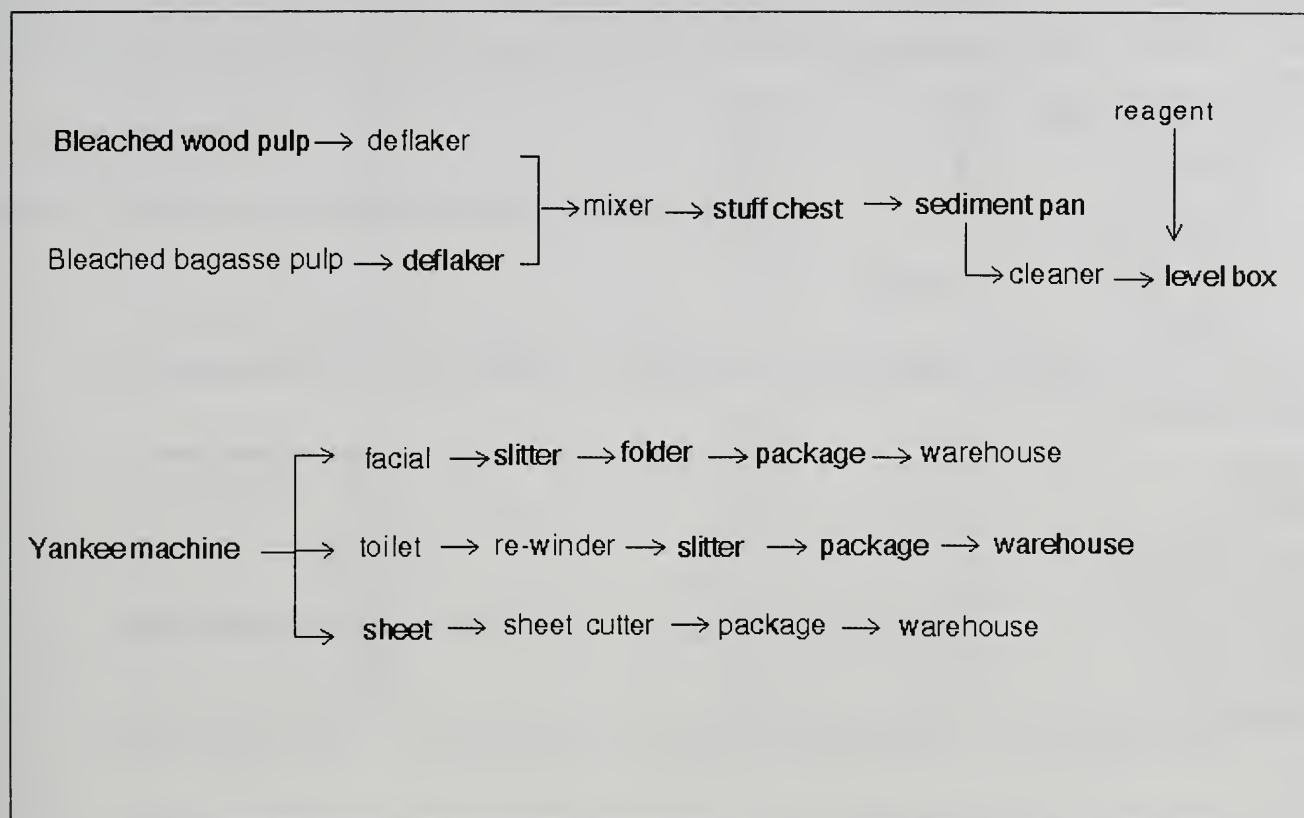


b. Key techniques

1. Choose appropriate retention reagent, neutral sizing reagent, filler, colorant, and inject them on the process at the right point.
2. Control the freeness and furnish of wood pulp and bagasse pulp.
3. Avoid over-refining and damaging the fiber of bagasse pulp

C. Household tissue

a. Flow sheet



b. Key techniques

1. Bagasse pulp contains lots of fines, semi-fiber and short and stunted fibers that make paper rough and crispy. To overcome these defects, we deflake the bagasse pulp by double disk refiner in higher consistency than normal, with some reagent added, to avoid shortening the bagasse fiber.
2. Impingement angle of Crepe doctor, soften reagent and lower biting of pulp can help improve the hand feel of the tissue
2. Quality of Bagasse Paper

Guitang's bagasse paper families are made up of cultural papers like offset printing paper, writing paper and sized paper, and household tissues such as facial, napkin, toilet roll and sheet tissue. All of the bagasse papers are superior to the national standards.

Quality standards of bagasse offset printing paper

Item	Unit	National Standard (QB 1012-91 Class A)	Test result
Basis weight	g/m ²	60.0±3	59.5
Surface absorb	g/m ²	≤30.0	21.3
Profile wrapping resistance	times	≥12	12
Smoothness Roll side	S	≥40	66
Felt side	S	≥40	53
Two-sided	%	≤20	19
Dirt 0.2-0.5mm ²	piece/m ²	≤60	11
>0.5≤1.5mm ²		≤5	0
>1.5mm ²		0	0
Thickness	mm	0.075±10%	0.079
Profile thickness variance	%	≤10	3
Brightness	%	≥87	92
Non-transparency	%	≥84	86
Breaking length	m	≥3200	3790
Profile stretch	%	≤2.2	2.1
Solid content	%	8-15	10
Moisture	%	4-9	6.2

Quality standards of tissue napkin

Item	Unit	National Standard (ZBY 32032-90 Class A)	Test result
Basis weight	g/m ²	12.0±1.0	12.5
Softness	mN	≤85/two ply	82
Absorbency	mm/100g	≥20	55
Tensile	mN	≥650	1120
Brightness	%	≥85.0	90.4
Pore	Piece/m ²	≤5	2
Felt side		0	0
Two-sided		0	0
Dirt 0.1-1.0mm ²	Piece/m ²	≤20	3
>1.0≤2.0mm ²		0	0
>2.0mm ²		0	0
bacteria	Piece/g	≤200	<10
Coliform bacteria	Piece/100g	≤30	<30
Pathogenic bacteria	Piece/g	0	0
Moisture	%	5-8	6.5

Pollution control

An operating paper mill uses thousands of tons of water every day and turns it into waste. The wastewater will produce heavy pollution if allowed to flow into the river without treatment. Guitang initiated research on wastewater treatment technology more than 30 years ago, paralleling that of paper-making. Due to its outstanding contribution to pollution control, Guitang was awarded Excellent Environmental Protection Enterprise of the State.

1. Alkali Recycling

A. Flow sheet

Down stream process for thin black liquor evaporation

Black liquor diffusion → magnetization → filter → thin liquor tank → pre-heater #3-4
→ evaporation effect #1-4 → medium liquor tank

Upstream process for thick black liquor evaporation

Medium liquor tank → pre-heater #1-2 → evaporation effect #3-4 → pre-heater #3-4
→ evaporation effect #1-2 → thick liquor pump → liquor burner
→ green liquor tank → lime slaking → re-caustizing tank → precipitating pool
↓
lime mud (CaCO_3)
→ recycled alkali solution

B. Key techniques

Thin liquor consistency: 6 Baumé at 20°

Pre-heated to: 40°

Thick liquor consistency: 25-27 Baumé

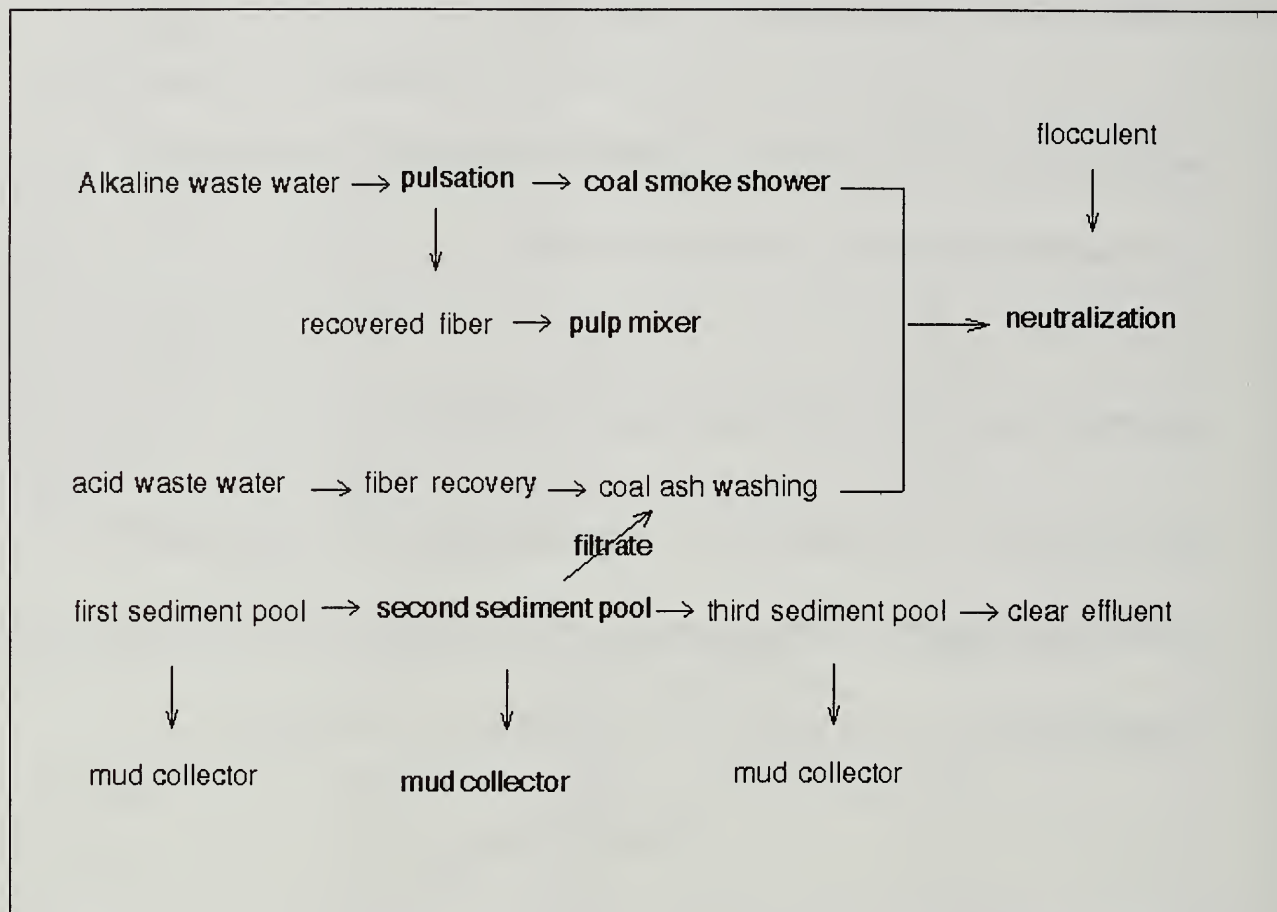
Pre-heated to: above 95°

Nowadays we can recover 80% of the alkali that is dosed into the pulp making line, which is good for us and good for the environment.

3. Middle section waste water treatment

We are adopting the CEH bleaching process for bagasse pulp on the middle reach of our paper making line. Waste water produced during chlorination and hypochlorite bleach is acid and clear, while during alkali extraction it is alkaline and dark brown, very hard to decolorize. Taking full advantage of their chemical natures, first we use the acid waste to wash the boiler coal ash and the alkaline waste to remove sulfur dioxide and dust from coal smoke, then we neutralize and clarify them before they are emitted in sewage.

A. Flow sheet



B. Waste water treatment assessment

This process can dramatically eliminate sulfur dioxide in coal smoke and organic compounds in waste water by the effects of chemical reactions such as neutralization, oxidation, reduction, absorption and physical effects like flocculation and precipitation.

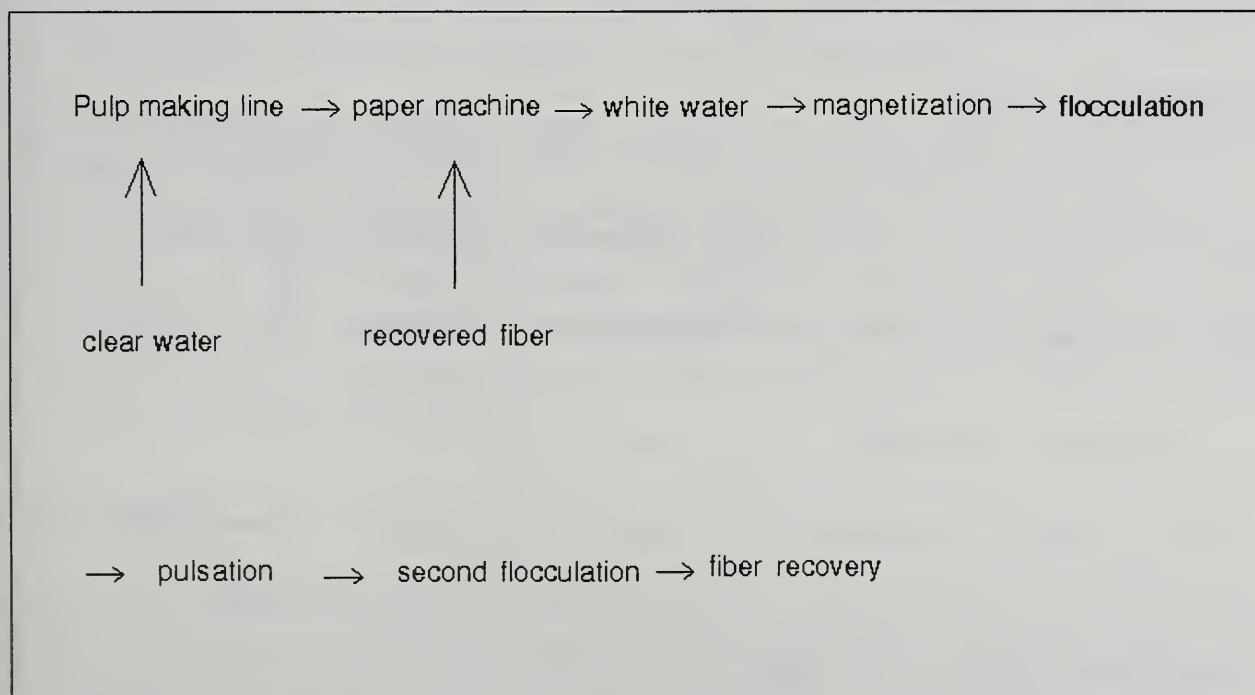
Comparison of water quality

Tested items	Pre-treatment		After-treatment	National effluent standards GB3544-92 Class II
	antacid	acid		
SS (mg/l)	300	200	20	200
CODcr (mg/l)	2500	1500	250	350
pH	11	4	7.5	6-9

3. White water treatment

A paper making operation produces huge amounts of white water, a milky suspension of fiber and filler. White water drainage not only pollutes the environment but also wastes natural resources. Guitang has developed a new process and equipment to treat it—the White Water Recovery New Process and Equipment acquired national patent in 1982 and a Certificate of National New Product. It can recover 99% suspension of white water. The separated fiber and filtrate can be totally re-usable for paper mill.

A. Flow sheet



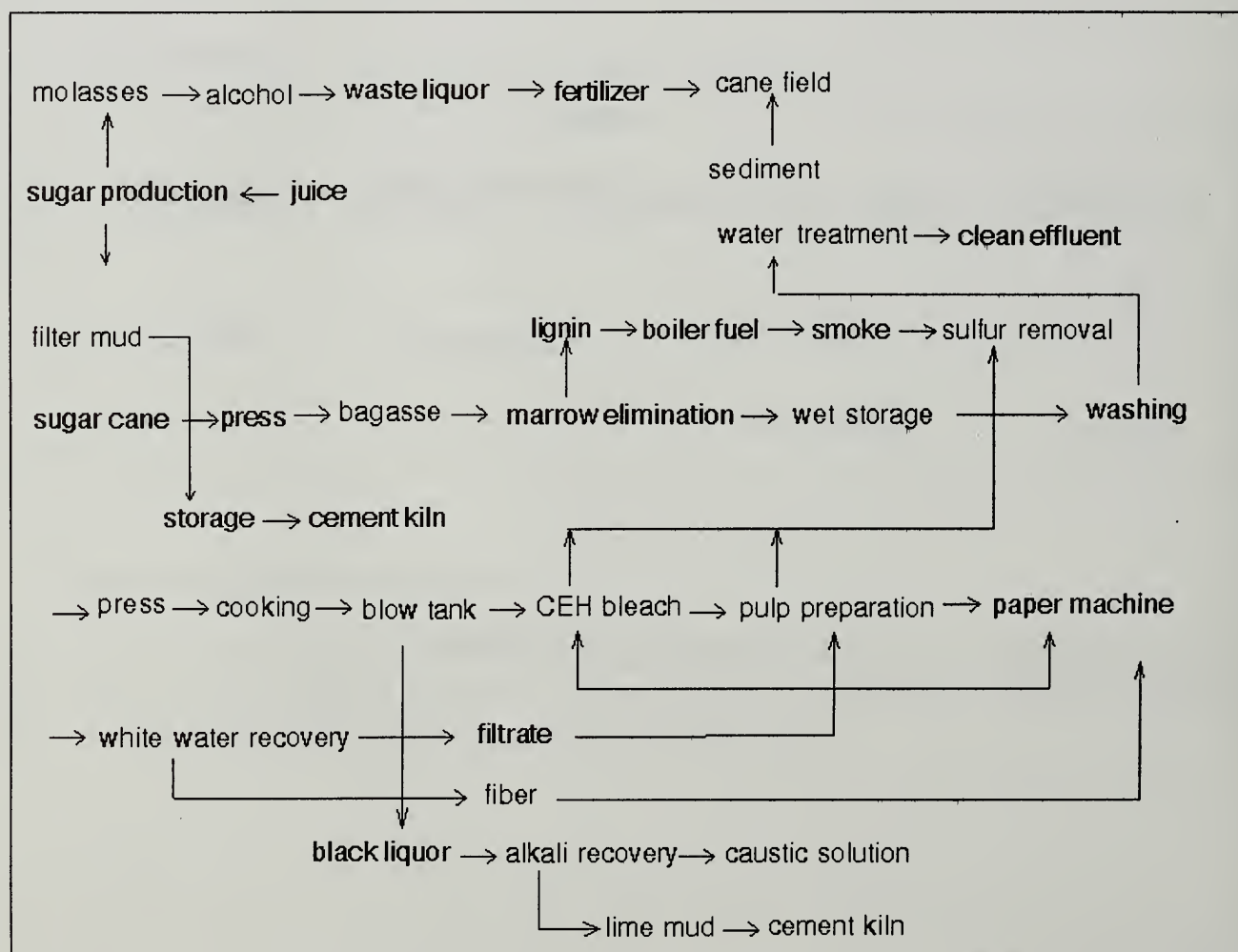
B. Treatment Result

Test Item	SS (mg/l)	COD _{Cr} (mg/l)	BOD ₅ (mg/l)	pH
Pre-treatment	1849	1187	561.8	7.28
After-treatment	19	76	40.7	7.18
National effluence standards GB3544-92 Class II	200	350	100	6-9

The equipment we invented is featured for low investment and operating cost, compact installation space, easy to operate and maintain, as well as durable and stable performance. We have 13 sets of this equipment commissioned in our paper mill. Investment for this equipment can be recovered within 1 or 2 years of operation.

Guitang has completed a closed circulation and treatment system for wastes in solid, liquid or gas form created during sugar, paper, and alcohol production and power generation. Guitang has achieved its goal of satisfying all emission requirements before 2000.

Diagram of comprehensive pollution control



Research topics in the future

The Paper Research Institute and the Post-doctorate Research Station of Guitang Technical Center will focus on the following subjects in the coming year:

- a. reagent for high quality cultural paper making from bagasse
- b. reagent for high quality household tissue making from bagasse
- c. Cl_2 & H_2O_2 bleaching process for bagasse pulp

Study on the above subjects is based on:

- a. There is no reported study on making high quality paper from bagasse. Geological allocation of natural raw material for paper decide that most of foreign countries are making paper from wood pulp, while China has to seek substitutes from wheat straw, rice straw, reed, bamboo, etc.
- b. There is no specialized paper chemicals preparation process and equipment for bagasse. Some foreign countries are leading the edge of research and production in this field, but they are orientated toward wood pulp.
- c. Research and application of reagent should be enhanced. China is starting in this realm quite rapidly in the recent years, though there is still a long way to go compared to some advanced countries on overall development, products variety, volume and quality.
- d. Specialized reagents for bagasse will open new space for paper industry and sweep technological obstacles for sugar cane comprehensive utilization.
- e. Low-chlorate or no-chlorate bleaching process is another subject that should not be ignored. In the 1980s, scientists from Canada, USA and Sweden found in succession poisonous dioxin compounds in water and sediment out of the CEH bleaching process. Nowadays, paper mills in China are considering introducing a ClO_2 and H_2O_2 bleaching process and relevant new technology. Expertise in Guitang Technical Center will cooperate with scientists from the National Lab of Pulp and Paper Engineering of Southern China Polytechnics University, aiming to define specific solutions for chlorate-free bleaching process for bagasse.

CONCLUSION

Making quality paper from bagasse is practical in technique and profitable in economy as long as technical problems for quality improvement and pollution control are properly solved. Experts and technicians of the State-approved Enterprise Technical Center and the Post-doctorate Research Station in our company have achieved some positive results in this field in terms of technological research, technical innovation and application, which have already enabled us to make paper and tissue from bagasse. Application and dissemination of these special technologies will save forests, benefit hundreds of sugar mills and contribute to the environmental industry of the world.

ULTRAFILTRATION OF CLARIFIED CANE JUICE USING SPIRAL AND TUBULAR POLYMERIC MEMBRANE CONFIGURATIONS

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ABSTRACT

The advantages of spiral polymeric membranes for the filtration of clarified cane juice are enhanced by combining the spiral polymeric membrane system with a tubular polymeric membrane system. By processing the retentate of the spiral system with a polymeric tubular system the overall yield of this membrane filtration operation is increased. Satisfactory and consistent performance of the polymeric spiral and tubular membranes was demonstrated processing clarified cane juice at high temperatures in a sugar mill environment. The performance data from commercial scale polymeric spiral membrane systems and polymeric tubular membrane systems will be displayed.

INTRODUCTION

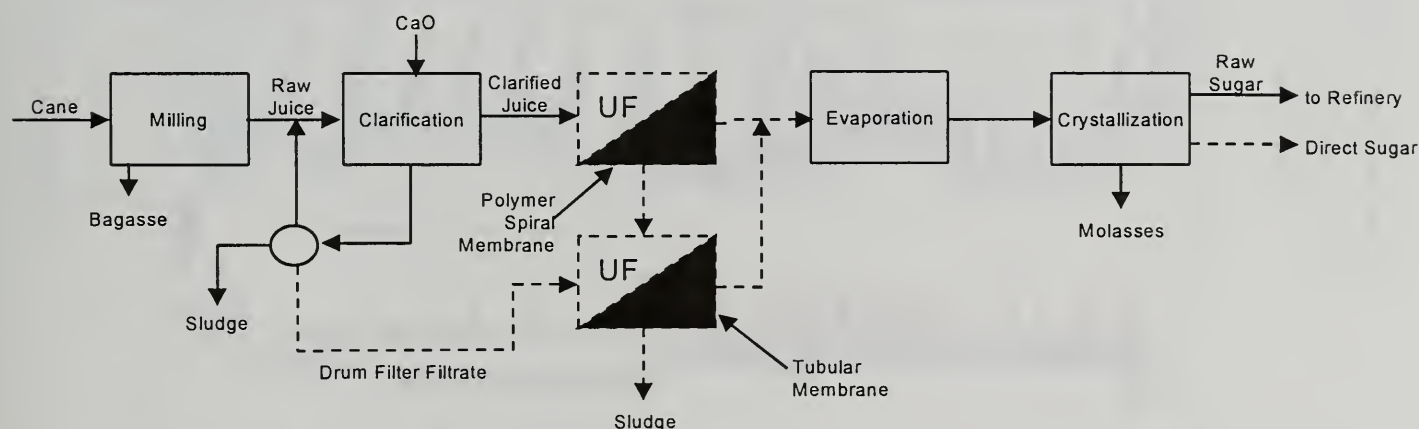
For the past several decades Koch Membrane Systems has been a major global leader in introducing and integrating membrane technology into the sugar processing industries. Koch has conducted pilot testing and installed large commercial units into the sugar processing industries around the globe. Based on their many years of commercial dextrose experience, Koch has been aggressively pursuing the use of membranes in the sucrose processing industry. Since the mid 1990's Koch has been active with sucrose pilot trials and semi-commercial plants in North America, South America, Asia, Australia, and Europe.

As a result of this testing initiative, Koch Membrane Systems has developed an 8" diameter spiral polymeric membrane module for use in high temperature (up to 98 °C) sugar applications. Koch also offers a ½" tubular polymeric product which has excellent temperature and chemical stability and is well suited for processing higher solids streams at sugar mills and refineries.

Ultrafiltration in Sugar Manufacture

Figure 1 shows a generalized flow schematic using spiral polymeric ultrafiltration to process clarifier overflow at a cane sugar mill. A 100-micron automatic back-washing prefilter is used to prevent plugging of the spiral membrane feed spacer. Retentate from the spiral membrane system is further concentrated with a polymeric tubular system. In addition, the tubular system may be used to process rotary vacuum drum filter filtrate, thus eliminating the need to send this stream back to the clarifiers for reprocessing. Ultrafiltration of the clarified juice stream can produce up to 15-25% capacity improvement in the evaporators and crystallizers at the raw sugar mill. Further, there is potential to use the improved quality sugar as direct consumption Plantation White Sugar.

FIGURE 1
Process Flow Diagram
for Cane Sugar with Membrane Technology



Membrane Process Data

Figure 2 shows process data from a spiral polymeric commercial scale demonstration plant operated during the past year. The spiral modules operated for approximately 1400 hours processing clarified cane sugar juice at 12-13 °Brix. Concentration factors ranged from 5-18X. Process runs were achieved with excellent repeatability at all concentration factors tested.

On average, cleanings were performed every 48 hours. Runs as long as 72 hours were performed at concentration factors of 5-7.5X. Cleaning cycles required approximately 2.75 hours for chemical circulation and an additional 2.25 hours for flushing. Cleaning cycles achieved excellent restoration of the clean water flux of the membrane system and maintained consistent performance of the system throughout the crushing season.

FIGURE 2
Koch 8" Spiral Membrane System, 1999-2000
Clarified Cane Juice, 12-13 °Brix

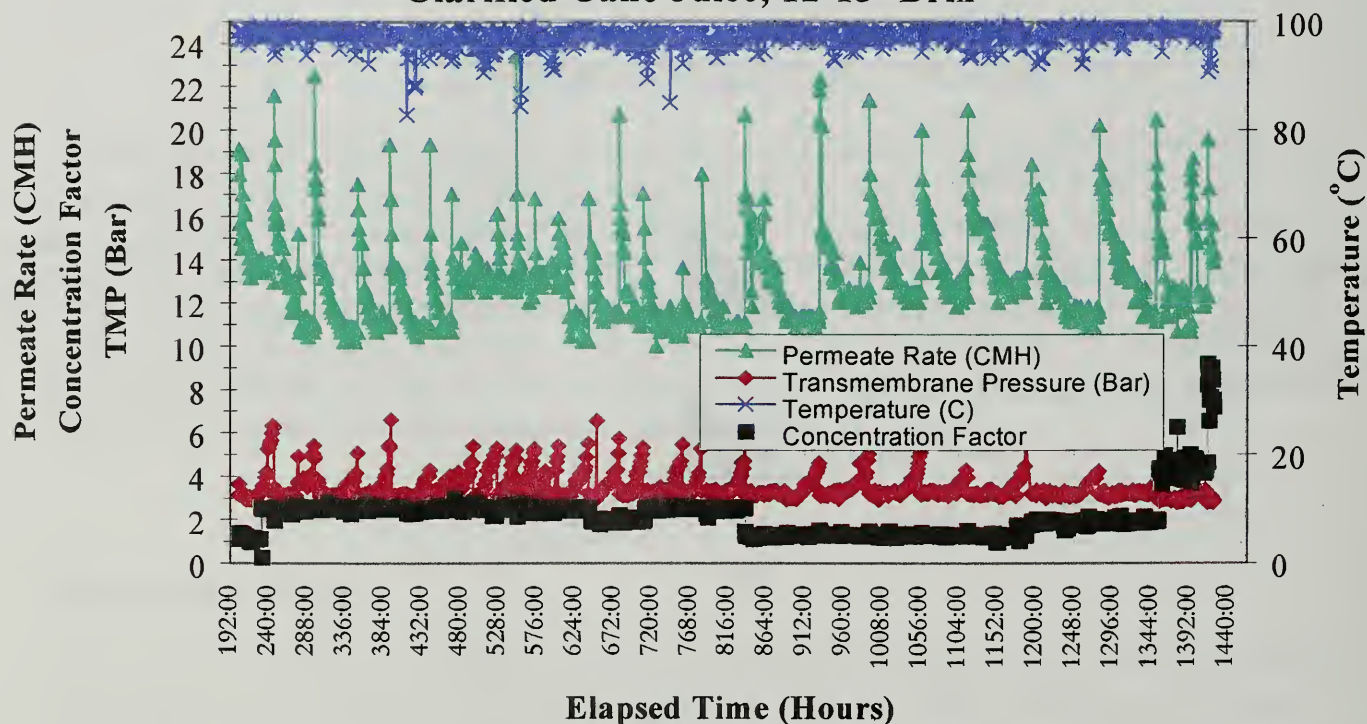


Figure 3 shows average process data from a second spiral polymeric commercial scale demonstration plant operated during the past year. The spiral modules operated for approximately 200 hours processing clarified cane sugar juice. Concentration factors ranged from 5-10X. On average, cleanings were performed every 24 hours. Cleaning cycles required approximately 2.75 hours for chemical circulation and an additional 2.25 hours for flushing. Each run began at high permeate rates (90 CMH) and decreased to a feed flow rate (40 CMH) by the end of the run.

FIGURE 3
Koch 8" Spiral Membrane System, 1999-2000
Clarified Cane Juice, 20 °Brix

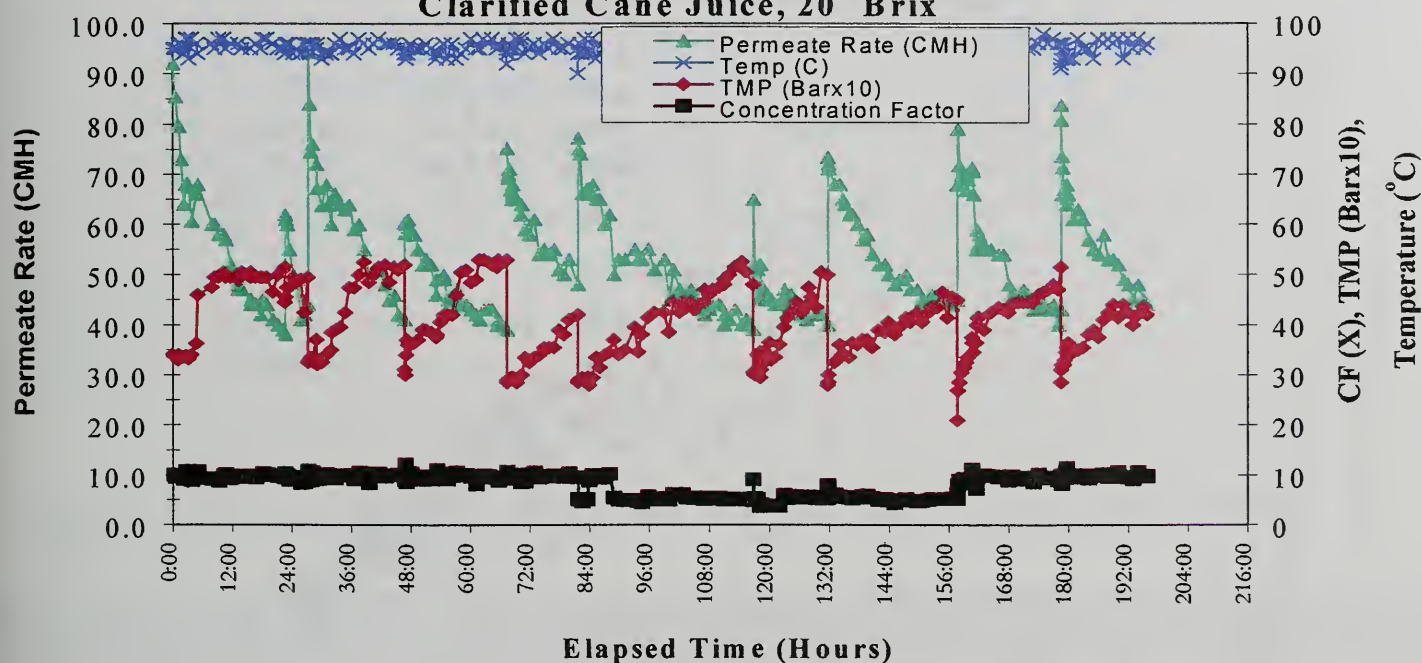
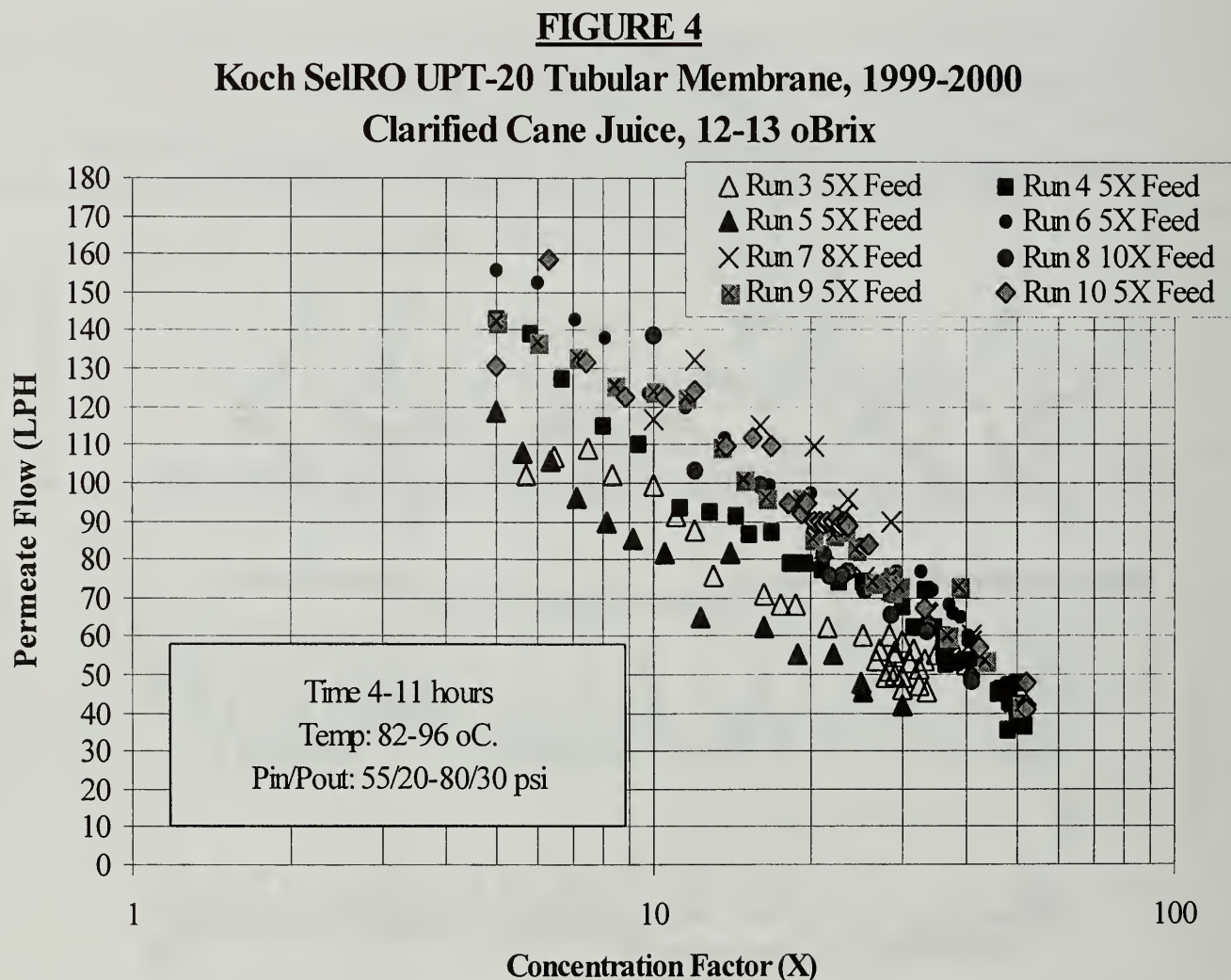


Figure 4 shows process data from pilot scale testing of Koch T-20 tubular membranes on clarified cane juice concentrated to 5-10X using a 4" diameter Koch high temperature spiral membrane. The tubular membranes were operated in batch mode for up to 11 hours per run. Total time processing juice during the testing was approximately 70 hours. Concentration factor was increased during each run from 1-10X in the tubular skid with a resulting total concentration factor of up to 50X (98% recovery of sucrose). Cleanings were performed daily in the batch mode.



Analytical Results

Koch spiral and tubular polymeric membrane systems can achieve nearly complete rejection of suspended solids and turbidity. Further, significant reduction in color, dextran, total polysaccharides, and starch can be achieved. Analytical results from polymeric spiral testing on clarified cane sugar juice are shown in **Table 1**. This data represents average values from approximately 2000 hours of process time.

Analytical results from polymeric tubular testing on concentrated clarified cane sugar juice are shown in **Table 2**. This data represents average values from approximately 100 hours of process time.

TABLE 1: Summary of Spiral Membrane Analytical Data – Clarified Cane Juice¹

Parameter	Average Feed	Average Permeate	% Reduction
Color (IU)	11,000	9,900	10
Dextran (ppm) ²	173	0	100
Total Polysaccharides (ppm) ³	3,400	810	76
Starch (mg/kg) ³	251	91.6	63
Brix	13.26	12.86	3.0
Pol	11.29	11.26	0.27
Purity (%)	85.20	87.55	(2.7%)
Turbidity (NTU)	200-400	0.2-0.8	99
Suspended Solids (%) ⁴	<1	0	100

¹Concentration Factor = 7X

²Haze Test

³From 4" Spiral Testing, 250 Hours Testing

⁴Centrifuge 10 mL sample

TABLE 2: Summary of Tubular Membrane Analytical Data – Concentrated Clarified Cane Juice¹

Sample	Brix	Pol	Purity (%)	Color (IU)	Color Rejection (%)	Turbidity (Abs.)	Turbidity Rejection (%)	Dextran ² (ppm)	Dextran Rejection (%)
Retentate	17.2			25,150		16,900		1,925	
Permeate	15.3	57.3	87.5	12,100	51.9	550	96.8	0	100

¹Concentration Factor = 7-50X

²Rapid Dextran Test (Modified Haze Test), 7-14X

NEW APPROACHES TO CRYSTALLIZATION THEORIES

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"Wisdom is one thing, it is to know the thought by which all things are steered through all things"
Herakleitos (544-483 BC)

"The spinning whirlpool which is called necessity, is the birth cause of everything" Democritus (460–70BC)

ABSTRACT

Two fundamental crystallization theories are briefly described: The theory of the adsorption layer, which deals with the crystal surface, and the diffusion theory, which considers phenomena occurring at the crystal solution interface. Another approach is proposed based on chaos and complexity theory. The chaos and complexity theory deals with the nonreversible thermodynamics of non-equilibrium conditions. It is correlated also with the concept of entropy, which being a measure of disorder and uncertainty, becomes the cause for the creation of new patterns of mass and energy dissipation. These all being called "*dissipative structures*" from the 1977 chemistry Nobel laureate Ilya Prigogine. Apart from the different levels of concentration, viscosity, temperature, pressure, supersaturation etc. of the mother liquor, there are also the different impurities which influence sucrose crystal growth morphology, modifying the habit of the crystals. In the same strike it is highly improbable that one crystal of sugar examined in the atomic scale, will be identical to another. It has been said that snowflakes are unique and no snowflake can be identical with another. The same seems to be valid for the sugar crystals. The sugar crystals, after drying, are in equilibrium with the environment, but they bear in their surface, examined under an electron microscope, with dislocations and other irregularities of their crystal lattice the irreversibilities of their growth. The sugar crystal is an "equilibrium structure" but bears on its surface and on its inner structure the fingerprints, the history of a "dissipative structure". The sugar crystal is a frozen, immobilized, crystallized irreversible "dissipative structure". It is the 3-D configuration and materialization of a transient structure. The pulsating character and mechanism of crystallization presents similarities to the Belousov-Zhabotinski reaction. To simplify and explain better the molecular dynamic simulation of sucrose crystallization, the application of an eleven dimension model is proposed. The four forces of nature (gravity, electromagnetic, weak and strong) are in interaction during industrial crystallization. Problems of conglomerates and poor CV of continuous vacuum pans with stirrer in comparison to the discontinuous vacuum pans with stirrer are discussed and a solution for improvement is proposed based on the logic of chaos and complexity theory.

INTRODUCTION

The viewpoint has been expressed that the science of the 20th century will remain in the memory of humanity for only three things [37]:

- Theory of relativity (*Hermann Minkowski*, (1864-1909) *Constantin Caratheodory* (1873-1950), *Albert Einstein* (1879-1955), Formula: $E = mc^2$, curvature of space and time through gravity, (*Riemann* geometry) Range of application: macrocosmos.
- Quantum mechanics *Max Plank* (1858-1947), *Werner Heisenberg* (1901-1976), *Niels Bohr* (1885-1962), *Louis de Broglie* (1892-1987) *Paul Dirac* (1902-1984), *Erwin Schrödinger* (1887-1961), and many others, only mathematical formulas, no visual configuration possible maybe a pictorial approach through the “*Richard Feynman* (1918-1988) diagrams.” Range of application, microcosmos, particles below 10^{-8} cm, that is below 1 Å or 10 nm Formula: uncertainty relations of *Heisenberg* $\Delta x \cdot \Delta p \geq h$ and $\Delta E \Delta t \geq h$ (where x velocity, p position, E energy, t time, h *Planck's* constant = $6.626 \cdot 10^{-34}$ Js)
- Theory of chaos and complexity *Henri Poincaré* (1854-1912), *Boltzmann* (1844-1906), *George David Birkhoff* (1884-1944), *Kolmogorov* (1903-1987), *Edward Norton Lorenz* (1917-) [21], *Li & Yorke* [17], *Benoit Mandelbrot* [22-26], *Ilya Prigogine* (1917-) [30-35] and many others, fractal geometry [29, 37, 38]. Range of application, microcosmos and macrocosmos.

All three theories have a common denominator: energy. Practical applications and scientific uses of relativity theory include atomic energy, cosmology. Practical applications and scientific uses of quantum mechanics include the basis of modern development in chemistry, molecular biology and electronics and the foundation of the technology that has transformed the world in the past half-century, semi-conductors, catalysts, physics of crystals, computers, lasers, etc.[45].

Applications and scientific uses of chaos and complexity theory and of the related fractal geometry have been reported in cosmology and astronomy [43, 48], in seismicity and tectonics, in soil properties, in fracture networks, in oil and gas reservoir porosity, in transport of fluids, in porous media, in aquifer hydraulic conductivity, in the modeling of population and of biological growth [42], in the modeling of plants [36], in laser optics, in fluid flow, that is in hydrodynamics, in chemical kinetics [33a], in crystal growth, in conglomeration of particles, in superconductivity, in cardiology, in the construction of pacemakers to confront cardiac arrhythmies, in pathology to explain the growth of carcinogenic cells, and in the stock market and weather forecasts [25]. Other uses of this theory are reported in telecommunications (transfer of codified messages which are a mixture of chaos and order), in the production of pharmaceuticals with large active surfaces, in the interpretation of morphogenesis and of the codification of DNA. *Christodoulou* has proposed the application of this theory in the study of *Cercospora* and other diseases [13], in the study and evolution of expert systems in a sugar factory [12], in food science technology [14], in agricultural science [15], in energy economy and in sugar technology [2-5, 16, 44], and proposed consideration of this theory as an evolution of thermodynamics for non-equilibrium conditions [16].

A recent application of fractal geometry is referred to by Amalgamated Research Inc. (ARi) with the ARi fractal distributor in their chromatographic separator [53, 66]. Fractals are considered to be “chaotic attractors”.

A *fractal* is a geometric shape that can be separated into parts, each of which is a reduced-scale version of the whole. Fractals are objects with self-similarity, which parts are small repetitions of the whole object [66]. We must distinguish between fractals and multifractals. In fractals the “generator” is of constant dimension, in multifractals the “generator” is changing in dimensions. The characteristic of fractal geometry is that its dimension is not an integer number (1,2,3,4) but fractional, and it is expressed by a recursive algorithm [16]. One fractal is a geometric shape in space or in time having a fractal dimension bigger than its topological dimension [66].

Related to the chaos and complexity theory is *fuzzy logic* which has found many applications in automation systems, e.g. in home washing machines as well as in control and automation of a sugar factory and especially in pulp driers and drums for cement production (smart, expert systems). The “*fuzzy logic*” of chaos together with the probabilistic inference will give rise to new computational tools for the management of complex systems [12], [67].

The basic common characteristic of the two theories of *quantum mechanics* and of the theory of *chaos and complexity* is the principle of *uncertainty* whose forefather seems to be *Herakleitos of Ephesos* (500 B.C.) called the *Obscure or Dark*, who in a seminal way expressed the principal of uncertainty of indeterminism, and of fuzzy logic saying : “*We step and do not step into the same rivers, we are and are not*” and “*The wise is one only. It is unwilling and willing to be called by the name of Zeus*” [10].

“*All things are one*” and “*Wisdom is one thing, it is to know the thought by which all things are steered through all things*” that is the foundation of the concept of complexity. “*The hidden harmony is better than the open*” and “*Nature loves to hide*” This is a prelude to the concept of *entropy*. *Herakleitos* expressed also the principle of *irreversibility* saying: “*You can not step twice into the same rivers, for fresh waters are ever flowing upon you*” and the principle of probability: “*Time is a child playing dices, the kingdom belongs to this child*” *Einstein* expressed the opposite idea in his famous God-does-not-play-dice dictum [54]. *Einstein* was horrified by this random, unpredictable element in the basic laws. Most other scientists, however, accepted the validity of the new quantum laws and the Heisenberg uncertainty principle. No longer did tiny particles have a defined position and speed. To the contrary, the more accurately you determined the particle’s position, the less accurately you could determine its speed, and vice versa. The world has changed far more in the past 100 years than in any other century in history. The reason is not political or economic but technological -- technologies that grew directly from advances in basic science. Clearly, no scientist better represents those advances than *Albert Einstein*, TIME ‘s Person of the Century [45].

Quantum theory and relativity can’t work together, but M theory, which incorporates the idea of strings, could meld the two at last [46]. Conventional physics has four dimensions including time. M-theory, which can be considered as an offspring of the chaos and complexity theory, suggests that there are as many as 11 dimensions -- but the extra dimensions are almost certainly detectable only at subatomic scales [46]. M theory is depicted in Fig. 1.

However, the results and their impact of the existence and action of all these 7 surplus dimensions are detectable not only in subatomic scales (below 10^{-8} cm) but in the macrocosmos as well, because in these 7 hidden inside the nuclear dimensions and in the chemical bonds are included all the properties and chemical characteristics of the different elements and molecules, which make the complexity of our world.

It is necessary to give some definitions about the meaning of *deterministic chaos*, *pathetic chaos*, *chaotic behaviour*, *bifurcations*, “*dissipative structures*” (invented by Ilya Prigogine). We intend to propose these *dissipative structures* as the model for the sucrose molecules association and pro-nucleation in clusters before crystal growth, in the labile phase before solidification, that is, before crystallization.

We intend in this account to refer briefly to the already known crystallization theories of adsorption layer and diffusion and propose a new approach by means of both the theory of chaos and complexity and quantum mechanics. We intend also to discuss why not even one sugar crystal seems not to be, examined under an electron microscope, absolutely identical with another and why sugar crystallization growth shows clearly a pulsation nature [47]. Some practical conclusions are summarized at the end.

The chaos and complexity theory, definitions and concepts

Chaos mathematically is determined as the unpredictable and apparently random behaviour of a deterministic system that is extremely sensitive to infinitesimal changes in initial parameters. The central idea is that self-organization is almost inevitable in a wide range of systems, both natural and man-made. The essence of chaos theory is that certain phenomena involve so many factors that they are inherently unpredictable. Reason: in systems governed by the mathematics of chaos, small events have big consequences. The best that scientists can do is recognize that the world's chaos follows certain patterns. Complexity theory examines the systems that lie between the two states. We think of a complex system as one that is probably never in equilibrium and always in transition, a system with many interlocking parts that are not easily described by simple arithmetics [16]. The concept of chaos is characterized by nonregularity, difficulty to distinguish between cause and result, apparently irregular (random) behavior and uncertainty of prediction [16].

We must distinguish between *pathetic chaos*, where the restoration of order is impossible or although having limited possibilities, the cost is high and brings about even greater disorder in the surroundings and also in the universe as a whole; and on the other hand in a chaos which is found in a dialectical relation with order, which is able to produce order because it includes structures of order. This last organized or *deterministic chaos* bursts into science and is under discussion in our days [48]. Prigogine also distinguishes between *pathetic entropy* and *deterministic entropy*.

Complexity is often called “*antichaos*”. *Chaos* and *complexity* should be considered supplementary concepts, as the two opposite faces of the same coin. *Chaos* is the Unity, the Eternity or the Oneness, the Whole, the Time before Existence, the Singularity, the *One* without limits of space and time the archetypal mist or cloud, the formless Matter supposed to have existed before the creation of the universe before Time and Space. *Complexity* is the *Many*, the Multiplicity, the

Variety, the Diversity, the Biodiversity, the Life, the Irreversibility, the Temporary, the Chemistry, the Engineering, the Universe, the Real World (organic and inorganic). The *Cosmos* which means in Greek order, beauty, universe, a well ordered whole, and system (contrasted with chaos), a sum total of experience [16]. But the early Greek philosopher who expressed in a seminal way the contemporary ideas of chaos theory is *Democritus* (460-390 B.C.) who said: "*The spinning whirlpool which is called necessity, is the birth cause of everything*". The whirlpool is the symbol of chaotic movement. *Democritus* is the forefather of the atomic theory and of the 1st law of thermodynamics while *Herakleitos* is the forefather of the 2nd law of thermodynamics and of the related concept of *entropy*, who is saying (*Nature loves to hide*) and of the principal of irreversibility (*you can not step into the same river twice*).

The word "Chaos" certainly means the "gape" or "yawn", the Orphic "big enormous without limits chasm" [57]. *Jacob Grimm* compared it with the Scandinavian Ginnunga Gap [55]. The word chaos is met for the first time in the Theogony of *Hesiod* 700 B.C. Said *Hesiod*: "*In the first beginning was Chaos*."

Hesiod mentions the two great cosmogonical figures, *Chaos* and *Eros*, and *Gaia*, which is the only material thing in the drama of creation. The concept of *Chaos* represents a distinct effort to picture the beginning of things. It is not a formless mixture, but as its etymology indicates, the yawning gulf or gap where nothing is as yet but bring in it the spermata of everything [55]. In our contemporary terminology *Chaos* could symbolize *Energy*, *Eros* could symbolize the *interaction* that is the mutual attraction and repulsion of all the four forces of Physics (gravity, electromagnetic forces, weak and stark interaction) [59] or the *Entropy*, the *Logos*, or the sweetness (we know that the sweetness is manifested by an electrical voltage of 20,000 Volts/cm [39]. *Gaia* could mean the creation of the material world in all its diversities and complexities. The figure of *Eros* was mentioned to explain the impulse to production which gave rise to the whole process. "*Men do not know how what is at variance agrees with itself. It is an harmony of opposite tensions, like that of the bow and the lyre*" and "*The one is made up of all things, and all things issue from the one,*" said *Herakleitos*.

The truth which *Herakleitos* proclaimed was that there is no One without the Many and no Many without the One. The world is at once one and many, and it is just the "opposite tension" of the Many that constitutes the unity of the One. The unity of opposites was the central doctrine of *Herakleitos* [55].

For the concept of entropy and for the famous formula of Boltzmann which combines the One and the Many see Appendix A. For the etymology of the world chaos see Appendix B.

In the 1980s researchers learned that for many real systems the myriad uncooperative complications of nature cause observations to disagree with predictions extremely quickly. You can, for example, take all the temperature, pressure and wind-speed readings you want, but you just won't have enough information to forecast the weather accurately more than seven days ahead. The reason is that the effects of tiny perturbations, can build much more rapidly than scientists had realized, altering the weather in unforeseen ways (Butterfly effect). Systems that tumble rapidly into unpredictability are aptly termed "chaotic". Chaos inhabits the gap between the perfect predictability of a frictionless pendulum and the pure randomness of rolling dice. A chaotic

system is not random. Because each event affects the one that follows, some combinations are more likely than others [49]. Chaos produces entropy, deterministic entropy evolves also in time and it is proportional to time, Chaos, entropy equilibrium, non-equilibrium, energy-entropy, free energy, fractals are connected through the Gibbs formula.

$$\Delta F = \Delta H - T_0 \Delta S \quad (1)$$

This formula can be modified as following

$$\Delta F = \Delta H - T_0 \Delta T^2 dt \quad (2)$$

where F = free energy, H = enthalpy, T_0 = temperature, S = entropy, t = time, this formula represents a dynamic system which gives deterministic chaotic solutions that is fractals [16]. An infinitesimal change in temperature, pressure or volume will create instability and therefore a different course.

Christodoulou proposed to consider chaos as a function of entropy and fractal geometry to be understood as a dynamic system of entropy evolution. The formulas expressing fractal geometry and entropy are similar [16] because they express energy transfer. Deterministic chaos is a dynamic system which evolves in time. More about the mathematical and thermodynamic approach to the chaos and complexity theory and the connected fractal geometry is given in the literature [11-17, 21-26, 29-38, 42-43, 48, 49, 54, 61, 66, 67].

Thermodynamics of non-equilibrium, oscillations, bifurcations and dissipative structures

The most important scientist of chaos is considered the Belgian chemistry *Nobel* laureate 1977 *Ilya Prigogine*, born in Moscow in 1917. His engagement with a basic problem of physics turned him towards the study of thermodynamics. Convinced that the thermodynamics of equilibrium cannot describe the processes in which time is expressed, *Prigogine* was occupied with the thermodynamics of non equilibrium. This has two branches. The first is the linear where the behaviour of systems near equilibrium is described, and the second is the nonlinear, which is referred to systems apart from equilibrium. In these situations where the linearity collapses and the symmetrical relation between flows and forces ceases to exist, *Prigogine* found that stable situations can become unstable, that is fall into chaos. But in a strange way, although the fluctuations are evolving in a random way running a course to chaos, at some particular moment, one of these fluctuations is reinforced in such a way that the system chooses to quit the initial condition and to evolve to another, from a chaos state there emerges order [30-35].

From a macroscopic point of view it is necessary to distinguish between two types of structure: a) *equilibrium structures* and b) *dissipative structures*.

Equilibrium structures may be formed and maintained through reversible transformations implying no appreciable deviation from equilibrium. A crystal is a typical example of an equilibrium structure. Dissipative structures have a quite different status; they are formed and maintained through the effect of exchange of energy and matter in non-equilibrium conditions [30]. In our endeavour to approach the crystallization theories by the methodology which *Ilya Prigogine* has taught us, it is necessary to define the concept of oscillations, bifurcations and dissipative structures.

The *Belousov-Zhabotinsky* reaction, also called the chemical clock, consists of the oxidation of an organic acid (malonic acid) by potassium bromide in the presence of a suitable catalyst, cerium, manganese or ferroin (Fig. 5, 6 and 7 of Ref. 16). Malonic acid $\text{HOOCCH}_2\text{COOH}$ is considered by some authors as a constituent of beet (page 130 [39] and page 277 [58]). In Figures 5 and 6 of Ref. [16] are given schematic representations of the *Belousov Zhabotinsky* reaction to show the different forms of temporal oscillation of the Br ion. In this reaction we see the following states: homogenous steady state, sinusoidal oscillations, complex, periodic states, subharmonic bifurcation, chaos, mixed-mode oscillations (chaotic and periodic), relaxation oscillations. In the x-axis is time, in the y-axis is the distance from equilibrium. According to *VanHook* (1981), sugar crystallization follows a chaotic pattern, which changes by change of temperature [52]. The rhythmic growth of sugar crystals, reminiscent of heartbeats, is shown in Fig.4 [47].

In Figure 7 is given the bifurcation diagram. In the x-axis is the bifurcation parameter (e.g. entropy) and in the y-axis are the different solutions (e.g. different forms of clusters). In the case of energy release (dissipation), entropy can be decreased at a bifurcation point, and this is the case for sugar crystallization, which takes place under heat and matter rejection (dissipation).

The best way to describe the “*dissipative structures*” is to quote *Prigogine*: “The dissipative structures are structures of non-equilibrium. This new Physics of non-equilibrium is the objective of many representations. It would be sufficient to say that today we know that matter under conditions of non-equilibrium behaves radically in another way, because the irreversible phenomena play in this case a fundamental role. One of the most spectacular aspects of this new behavior is the formation of new non-equilibrium structures, which exist so long as the system dissipates energy and stays in interaction with the surroundings. This is in obvious contrast to the equilibrium structures as e.g. the crystals which once formed could remain isolated and form dead structures without energy dissipation. The two scientific branches where the dissipative structures are investigated intensively, are hydrodynamics and the chemical kinetics. In the last time, came also the laser optics. A well known example from hydrodynamics is the *Benard* instability. By these experiment one liquid is heated from below. By adequate big temperature differences between the upper and low border surfaces of the fluid layer, are built eddies, which take with them milliards of particles. The non-equilibrium produces in this way correlations of large range. I would like to say that matter in equilibrium is blind, because every molecule sees only the next molecule, which is surrounding it. The non-equilibrium makes the matter seeing. Then one new coherence takes place. The multiplicity of non-equilibrium structures, which little by little are invented, brings some one in astonishment; they prove the fundamental creative role of irreversibility phenomena and of the time arrow” [33a].

The so called equilibrium structures like a sugar crystal bear the fingerprints of irreversibility on their surface and in their total structure. Every sugar technologist knows that after remelting and recrystallization the original quantity of sugar will not be recovered. Some quantity of sugar will be lost to the mother liquor. Equilibrium and reversibility is an idealization. In reality nothing is in equilibrium, nothing is reversible. Everything is in continuous change, in continuous flow. Motion and the evolution are eternal. *Everything is flowing*, according to *Heraklitos*, even in the case of sugar crystallization, which seems to be reversible.

Adsorption layer and diffusion crystallization theories.

The sucrose molecule contains 8 hydroxyl groups: three of them (*Mathlouthi* 1981) [63] can be involved in intramolecular hydrogen bond formation (Figure 12 *Lichtenthaler* (1991) Ref [27a], whereas the other five can be involved in intermolecular hydrogen bonds. The latter are responsible for sucrose crystal formation during the crystallization step or the solvation of sucrose molecules by water molecules during the dissolution step.

The fact that hydroxyl groups can form hydrogen bonds with water molecules accounts for the high solubility of sucrose in water. Even at room temperature, a saturated sucrose solution is made up of two parts of sucrose and one of water, at 100 C the saturated solution contains almost five parts of sucrose for each one part of water. In sufficiently diluted solutions all the hydroxyl groups are solvated with water molecules so that sucrose molecules can be considered as independent units forming the structure of clusters. As the solution is concentrated and the number of water molecules is no longer sufficient to form bonds with all the hydroxyl groups of all the sucrose molecules, aggregation between the sucrose molecules takes place. This gives rise to the associated structure. [27a]

Crystal growth is a very complex subject since one has to take into account phenomena occurring on the surface of the different crystal faces and at the crystal-solution interface. Two fundamental theories are summarized in the following: the theory of the adsorption layer which deals with the crystal surface, and the diffusion theory which mainly considers phenomena occurring at the crystal-solution interface. The aim of the adsorption layer theory is to explain what happens when a growth unit arrives at the crystal face to be integrated into the lattice. One can distinguish between ideal crystals (two-dimensional nucleation) and real crystals. It seems that in the case of sucrose crystallization the situation is more complex than that shown in Figure 12/11 Ref. [27a], because there is an exponential stretch (2) between the parabolic (1) and linear (3) one, which is assumed as two-dimensional nucleation between growing steps [27a].

Concerning the thermodynamic aspects of sucrose crystal growth, and, in particular, the activity coefficients and activation energy, reference to the exhaustive review of *VanHook* (1981) is recommended [52]. As is well known, *VanHook* carried out a great deal of research on many aspects of sucrose crystallization [51, 52]. The adsorption layer theory is based mainly on calculation of free energies which make part of thermodynamics of non-equilibrium.

We do not want to reject the adsorption layer and diffusion crystallization theories but to incorporate them into a broader set through the complexity theory and quantum mechanics. In reality, in sugar crystallization, we are at the edge between the realm of quantum mechanics because the dimensions of the sucrose chemical bonds are below 10^{-8} cm or 10nm and the molecular world with a little higher dimensions (cluster of about 80 molecules having a diameter of about 190 nm) that is we are at the edge between the microcosmos and macrocosmos.

Both the adsorption layer and diffusion crystallization theories are expressed by second grade partial differential equations which have only chaotic solutions having the form and appearance of fractals [56]. See also the continuity, partial differential equation of extraction (diffusion) given by *Schliephake* and *Buttersack*. This formula conducts again to a fractal (page 316 formula 6.31 of Ref [8]).

Discussion on Crystallization Theories

Buttersack and Schliephake pointed out the complexity of the beet extraction process [8], whereas *Mantovani and Vaccari* pointed out the complexity of sugar crystal growth [27]. (Figures 12/5, 12/7, 12/8, 12/9, 12/10, 12/11, 12/14, 12/15, 12/16, 12/17). The spiral growth of a sugar crystal (starting from a screw dislocation) characteristic of chaotic movement is shown in Fig.12/9 and in Fig. 5a [39].

Beet sugar molasses behaves like a newtonian liquid but cane sugar molasses and the massecuites and magmas of both beet and cane behave like non-newtonian liquids [7]. In the last case we probably have chaotic behaviour.

Mathlouthi and Genotelle (1996) have demonstrated the complexity of interactions between water, sugar and eventually impurities in oversaturated solutions during crystallization. The condition of the crystal surface and the nature of defects which come to be integrated into the molecules during crystal growth are worth considering as another aspect of crystallization. But if we observe the situation from the point of view of the liquid, remembering some properties of water solutions of sugar like hydration, diffusion, viscosity and interfacial tension, properties which have an influence on the molecule transport, it seems that the classical *Fick* theory of diffusion of sugar molecules is rather difficult to be applied. The interpretation of the literature and some hypothesis on the role of dissolving in the mechanism of crystal growth guides us to think that the *migration of water from the limit layer in contact with the crystal towards the rest of the solution is a predominant process to crystallization* [50]. The appearance of crystal nuclei in a oversaturated solutions of sucrose is preceded by the organization of hydrated molecules in clusters or “embryi” during a latent period said to be “pronucleation” [50].

The mechanisms of crystallization can be imagined as a course of “energetic obstacles” according to a scheme proposed by *Vanhook* (1977, 1981), where the following processes take place, convention, volume diffusion, absorption, diffusion on the surface, dehydration-dissociation, molecular alignment, counter diffusion, etc. The peaks and the valleys are different by low 45°C or high temperature [50, 52].

Sugar crystals have a fractal structure because being examined in different scales they show the same patterns of self-similarity and self-affinity. If you study a quantity of sugar macroscopically the crystals seem to be uniform. But if you examine them by means of a microscope their surface has such irregularities that we are reminded of the *Cheops* pyramid seen at close range [51]. The sugar crystals are a mixture of order and chaos.

It has been expressed that snowflakes are unique and no snowflake can be identical with another. One “seed” of dust of volcanic ash or one grain of impurity forms the nucleus of the crystal attracting molecules of water which freeze on its surface. The winds blowing between the changing layers of temperature pressure and humidity shape each snowflake differently. Although we are inclined to believe that snowflakes are formal stars with six rays, the International Commission of Snow and Ice has recorded many categories of snowflakes, each one formed under different conditions. Low humidity with little wind forms three dimensional snowflakes, while cooler drier clouds give birth to needle-like formations. Each snowflake is however one unique product of temperature and humidity, one natural fingerprint of the

atmospheric conditions. It has been estimated that there are at least one million different levels of temperature and humidity possible in the atmosphere, creating as a result five millions to the power of ten possible combinations [1]. Similar conditions and many more possible combinations exist in the case of sugar crystal nucleation and growth. Apart from the different levels of concentration, viscosity, temperature, pressure, supersaturation etc. of the mother liquor there are also the different impurities which influence sucrose crystal growth morphology modifying the habit of the crystals [40]. The inner structure of the sugar crystals is not also constant because their density and hardness are not the same. The same is valid for crystals of mineral [6]. Based on the internal symmetry and configuration, 230 space groups in the sugar crystal lattice can be distinguished which indicate the internal arrangement within the unit cell [41]. The application of stirrers in vacuum pans promotes the production of uniform crystals and avoidance of conglomerate formation.

The computer aided modeling of the molecular electrostatic potential and the molecular lipophilicity potential profiles of sucrose can explain the complexity of the original sucrose crystal growth (*Lichtenthaler et al* 1994, 1995, 1996) [18,19,20], (Fig. 2,3 of Ref [18]), (Fig 8,9,10,11) of Ref. [16] which originals are coming correspondingly from the Fig. 1,2,3,5 of Ref [19]. In fact the sugar crystals though crystallized, in the same monoclinic sphenoidal system, are never absolutely identical. Their surface is the pattern of chaos at work. Two individual beets or sugar canes are never absolutely identical if examined in their details. The same seems to be valid for all natural or man made products.

As shown in Fig 8, 9, 10, 11 of Ref. [16] in the molecule of sucrose there appear equipotential curves and the minimum of energy level corresponds to the solid condition. The configuration of these equipotential curves is based on free energy calculations. In fact, Fig. 8 represents the three energy minima from the adiabatic potential surface and for their generation temperature is not relevant. Temperature is only needed for conversion of the energy maxima into a population probability map (Fig.11 of Ref [16]), there the temperature is 300° K, i.e. 27° C [64].

With respect to the solution conformation of sucrose the first hydration shell around it was characterized (Fig.9 of Ref [16]): one water molecule is “trapped” in a bridge between fructose-1-OH and glucose-2-OH. As sucrose crystallizes without water, the “bridge-trapped” water molecule is certainly the most difficult (hence, the last) to be removed, this explaining the high oversaturation range of sucrose solutions before crystallization starts [18, 19, 20, 64].

The solution dynamics of, and the hydration around sucrose, were analyzed in terms of pair distribution functions. These indicate strong hydrogen bonding between all sucrose hydroxyls (as donors and acceptors) and water within a first, well-defined hydration layer (hydroxyl-oxygen-water distances 1.8-3.5 Å), whereas the acetalic oxygens are engaged to a lesser extent as H-bond acceptors. *The second hydration (>4Å) is rather diffuse and less pronounced, indicating those water molecules to be in a disordered state” say Lichtenthaler et Immel [19]. This disorder state of the second hydration layer (>4Å) seems to be the cause of the chaotic behaviour and of the diversity and irregularities of the sugar crystal habit.*

The heat of crystallization which is released is:

Temperature (° C)	25	60	90
ΔH, J/g	30.3	57.0	107.6 [28]

Baloh gives similar values in a graphical representation [4]. This heat evolved is not lost but helps to keep the solution boiling, thereby reducing the steam load in the sugar house [28]. Sucrose crystal growth in technical solutions does not follow a first order reaction even at high supersaturation values. The growth rate may follow a three-step model but the interactions in the solution, on the surface and at the integration in the crystal lattice are more complicated than in pure sucrose solutions. The order of the overall reaction increases with increasing nonsugar concentrations [27, p. 664]. This is a sign of deterministic chaotic behaviour.

What will be said subsequently is an expression of quantum mechanics: We must not imagine the sugar molecules as rigid bricks or as ricocheting billiard balls but as fuzzy clouds of probabilities, as dipoles with potentials which combine to form the first cluster of sugar molecules in the pre-nucleation. They obey odd rules of etiquette as they maneuver in a dance of mutual attraction and repulsion. They seek to rest in a nest of low energy releasing energy and matter. This nest of low energy can be a local minimum and not the absolute minimum. In this dance the non sugars interfere, impeding and modifying the structure of the sugar crystal meetings, that is the crystal habit. The *Brownian* chaotic movement of all molecules increases with higher temperatures and promotes this motion and collisions.

During crystallization, the entropy of the crystal is decreased, the impurities are eliminated and the heat of crystallization is dissipated. We can consider applying the terminology of the chaos and complexity theory to the sugar crystals as “*strange attractors*” of matter (sucrose) and as “*dissipative structures*” dissipating the heat of crystallization and the impurities of mother liquor. The self-organisation of the crystallization process is evident [42].

The sugar crystal after nucleation in the highly saturated mother solution and during crystal growth is found in conditions sometimes far from equilibrium and sometimes near equilibrium, but not in conditions of equilibrium.

Some molecules of sugar are dissolved from the already formed cluster and new molecules of sugar are deposited on the surface of the crystal lattice. The crystal surface during crystal growth is in continuous change. The sugar crystal formation is an exothermic reaction and takes place under dissipation (rejection) of matter and energy. This is a “*dissipative structure*” according to the chaos theory, as formulated by *Prigogine*, who coined this term [30]. *Herakleitos* formulated the same concept 2500 years ago with his famous “harmony of opposite tensions” which means harmonious coexistence through strife of the Many and the One.

The sugar crystals after drying are in equilibrium with the environment, but they bear in their surface, examined under an electron microscope, with dislocations and other irregularities of their crystal lattice the irreversibilities of their growth. This makes each sugar crystal unique. The sugar crystal is an “*equilibrium structure*” but bears on its surface and in its inner structure the fingerprints, the history of a “*dissipative structure*”. The sugar crystal is a frozen, a crystallized “*dissipative structure*”.

The ordered features of the sugar crystal are manifested in the self similarity in different scales of the angles and of the faces of the sugar crystal lattice, which belongs to the monoclinic sphenoid system. These angles and faces are the ordered constant features. The chaotic features of the

sugar crystal are manifested in the surface of the crystal, which has an extremely irregular, fragmented form in every scale of examination, that it has the form of a “fractal”. In this surface we see all the dislocations, vacancies and irregularities of the crystal lattice. In every deterministic chaotic system apart from the chaotic features, there are ordered features named mathematically “invariances” according to the terminology of *Mandelbrot* [25].

“The external shape of a crystalline substance is determined by its environment and conditioned by either physical or chemical factors or both. It is exceedingly difficult to predict the precise shape the crystal will assume, the only invariant feature being the angles of the faces with respect to each other. Individual faces are able to achieve growth rates differing from their neighbors and the overall growth rate merely represents the net growth rate of the sum of the individual faces” (*Frank Kelly* in his book “the sucrose crystal and its solution” published in 1975, quoted by *Mantovani* [27]).

The four forces of nature and sugar crystallization

As in every act of creation of new things, of order out of chaos, the four forces of physics are in action during industrial sugar crystallization: a) The *electromagnetic forces* between the sugar and water and non-sugar molecules during formation of clusters of about 80 molecules of sucrose having a diameter of about 190 nm [27, 50] and then when these clusters are dissolved and formed again in a continuous dance of mutual attraction and repulsion, we have the strange phenomena of quantum mechanics: of clusters of molecules seeking the low energy level dissipating energy and matter, in a condition of metastable equilibrium till the first solid aggregate is formed and then may again be dissolved. b) *Gravity*, the adverse influence of which in this case is limited by the application of stirrers and vacuum. In other cases of sugar technology the beneficial effect of gravity is used to promote separation as in the case of thickeners, filters or earth separators. c) The *weak forces* of gamma rays of measurement and control devices which are used in some cases to measure the density and oversaturation of the mother liquid and of massecuite during crystallization. The steam used to heat the vacuum pan during crystallization comes from the boiler house which burns fuel or gas or bagasse, a product of solar energy of the past. The solar energy is the product of weak forces that is of nuclear energy inside the nuclear kiln of the sun which is positioned a safe distance from us. d) The *strong forces* which dwell in the nucleus of all chemicals taking part in the play (sugar, water and non sugars). Instabilities, layer adsorptions, diffusions, oscillations, relaxations near and apart from equilibrium are taking part in the phenomenon.

The chaotic phenomena of addition, multiplication and boosting the initial quantum transfer of energy release and dissipation can explain the pulsating character and the springing capacity of crystallization as it is manifested in the surface of some sugar crystals (*natura facit saltus*). From the *chaos* of oversaturated liquid is formed the *order* of the nice sugar crystals. Nature is so creative that no sugar crystals with its defects and peculiarities is similar to another. Every crystal is unique, not even one crystal is perfect [47], examined under an electron microscope. Not only the four dimensions (3 space dimensions and time) are in play during crystallization but many more in the different chemical bonds in spin and in wave functions, in the intersaccharide torsion angles ϕ and ψ about the ϕ and ψ bonds etc. may be till eleven as teaches us the M-theory a new offshoot of the chaos and complexity theory. (Figure 1)

CONCLUSIONS

We can consider the crystallization of sugar as a visual (pictorial) representation of the forces of the microcosmos. It is a picture of what happens inside the chemical bonds, below 1 Å. This configuration in 3-D is never the same. It is unique each time. By applications of highly automated continuous vacuum pans the labour and energy demand are diminished but problems with conglomerates and sugar dust and the need for interruption every two weeks or so are not avoided. A discontinuous vacuum pan with a stirrer produces more homogenous crystals with better CV than a continuous vacuum pan with stirrer and even worse without a stirrer. The hydrodynamics of complexity can help us to improve this problem. (See Appendix C)

The theory of chaos and complexity can help us to understand better the complexity of the process of crystallization to solve practical problems: If we understand better we can also control better.

The chaos and complexity theory is the science of non-equilibrium of non-reversible thermodynamics, is the science of the whole which studies the question, that is how from the random, the unstable, the unexpected and the disorder there is created order and form. This is also the task of the science of a sugar technologist. From different raw materials (beet, cane, raw sugar, limestone, etc) which are characterized qualitatively by randomness, instability, fluctuations and disorder, he is obliged to produce during the campaign ordered products (mainly sugar, dry pulp, molasses and others) with high yield, low cost and of high quality and with conditions of sustainable evolution in relation to the environment.

“An entirely new technology will have to be developed to tap the high guidance and regulation potential of self-organizing systems for technical processes. The superiority of self-organizing systems is illustrated by biological systems where complex products can be formed with unsurpassed accuracy, efficiency and speed” *Nicolis G.* and others quoted by *Prigogine* [34].

In the past half century (1950-2000) the beet and cane sugar technologists and refiners have made in organization, energy economy optimization, automation and control, cost reduction of process technology, and in sustainability in relation to the environment giant steps. What has to be done for the Twenty First Century at the edge between the two millennia? To understand better, to improve further, “*to imitate nature's self-organizing biological systems where complex products can be formed with unsurpassed accuracy, efficiency and speed*” *Nicolis G.* and others quoted by *Prigogine* [34]

To increase efficiency in every sugar factory of the world imitating the best ones already existing, to decrease the cost even more, to pay higher attention to the human factor who plays the role of director in the drama of creation of sugar crystallization as we have described. It is impossible to apply any process technology without design, without construction, without supervision, without control. To feed the poor with low cost sugar in underdeveloped countries is a first important task.

Sugar crystallization being an exothermic reaction shows that nature wants to help us, offers “order for free”. In the book of *Paulo Coelho* the “Alchemist” is mentioned that “*if someone desires something really and ardently then the whole universe conspires to help him to realize his*

dream.” And in Portuguese: “*Se alguém tiver o desejo de atingir algo real, o universo inteiro conspirará para ajudar-lo a realizar o seu sonho*”. This is a nice way to express the new bond and the new dialogue with nature “*la nouvelle alliance*” which *Prigogine* advocates.

Acknowledgments. I would like to express my best thanks to Prof. Dr. h.c. *F.W.Lichtenthaler*, the SPRI science award recipient of 1994 (Helsinki), who has given me a very nice letter dated Nov.23, 1998 the permission to use his superb drawings of sucrose configuration by computers and has written to me that “retiring (taken by its literal sense) is what Formula 1 race cars do when they stop at the boxes to put on new tires”.

Dedications. I would like to dedicate this account to the memory of *Dr. Andrew P.VanHook* (1907-1990) SPRI Science Award recipient 1986, prolific writer and researcher on the subject of sugar crystallization and to the memory of *Dr. Margaret Alice Clarke*, (1942-1998) who died “upright” as managing director of SPRI and being an Active Member of the Scientific Committee of C.I.T.S. and many other activities.

Appendix A: The concept of Entropy, One and Many

There is one famous formula which combines the One and the Many - the formula of the Austrian Boltzmann (1844-1906) written also on his grave plaque.

$$S = K \ln W \quad (1)$$

where S =entropy, K = Boltzmann constant, \ln =logarithmus naturalis and W : probability (Wahrscheinlichkeit in German)

The proportionality factor K in the equation (1) is the gas constant referred to 1 molecule $K = R/N_L = 1,3803 \cdot 10^{-23} \text{ J/K}$ (R = gas constant, N_L = Loschmidt number)

By probability $W=1$ results $S=0$ this is the limit case of One. It is possible to express the probability of one event by numbers between 0 and 1 that is by fractals in which also are contained all the series of rational and irrational numbers that is infinite numbers. The dimension of entropy is given through the constant K , which represents the work which is produced when one molecule is heated by 1° Kelvin (or 1° C), that is energy divided by temperature

$$ds = dQ/T \quad (2)$$

In the cybernetics (system theory) entropy is applied in systems that have nothing to do with energy and temperature e.g. entropy of the speech, entropy of one society or of one organization. While thermodynamics permit (in closed systems), only the increase of entropy and in limited cases of reversibility, the constant value that is $\Delta S=0$, in cybernetics is typical the decrease of entropy. Through information the entropy of one system is decreased and many authors characterized the information as neguentropy. In the equation (1) examined under the previous assumptions, results the entropy proportional to the logarithm of number of microstates that realize one macrostate. In this case K is a number without dimensions and consequently entropy also is without dimensions [3].

In the case of sugar crystallization after the solidification that is after separation of the liquid and solid state the entropy of the liquid phase that is the mother liquor increases, the purity decreases but the entropy and the purity of the crystal is higher than the initial mother liquor before crystallization. The entropy of the whole remains constant and it can even be decreased by cooling. It

would be interesting to prepare a H, S (Mollier) diagram of sugar crystallization, based on the diagram of Baloh [65] p.55.

In case that one event is certain to happen we have probability one, in case that one event is certain not to happen we have probability zero. But it is possible to have all intermediate cases between one and zero for dynamic systems which are not stable e.g. the weather or the course of a sugar campaign. This is the basic concept of fuzzy logic.

Appendix B: Etymology of The Word Chaos (χάος in Greek)

Aristotle says that χάος comes from the verb χάοκω = yawn or the word χάσμα = gap, chasm, gulf.

If we add to χάος + όριον (limit, dimension) we have χώρος (space)

If we add to χάος + ροη + όν (flow + being) we have χρόνος (time).

Appendix C: A proposal for the confrontation of the problem of the worse coefficient of variation CV of sugar crystals produced by the continuous crystallization apparatuses.

The lower the coefficient of variation (CV) of sugar crystals the better. In Figure 12/143 VKT for the crystallization of white sugar (vertical tower) is shown that this apparatus has 4 crystallizing chambers with stirrers. Because of stirring, that is because of turbulent flow (chaotic movement) the formation of fine crystals is avoided. Nevertheless during the transport of the magma by gravity from one chamber to the next below, the conditions of flow change and the flow becomes linear (8: Magma transfer pipe), having as a result the formation of new fine crystals, which finally result in a higher CV of the sugar crystals. It is proposed that the correction of this undesirable phenomenon can be accomplished by the installation of a stirrer in the interior of pipe 8 or its shape changed in a way to avoid linear flow and to create turbulent flow (e.g. by means of a screw of Archimedes form, or of a static mixer, or of a fractal construction). The above has to be proved by experiments, but the main idea is patent pending. In Figures 12/139 and 12/140 is shown the turbulent flow which is achieved by stirring in the batch evaporating crystallizers.

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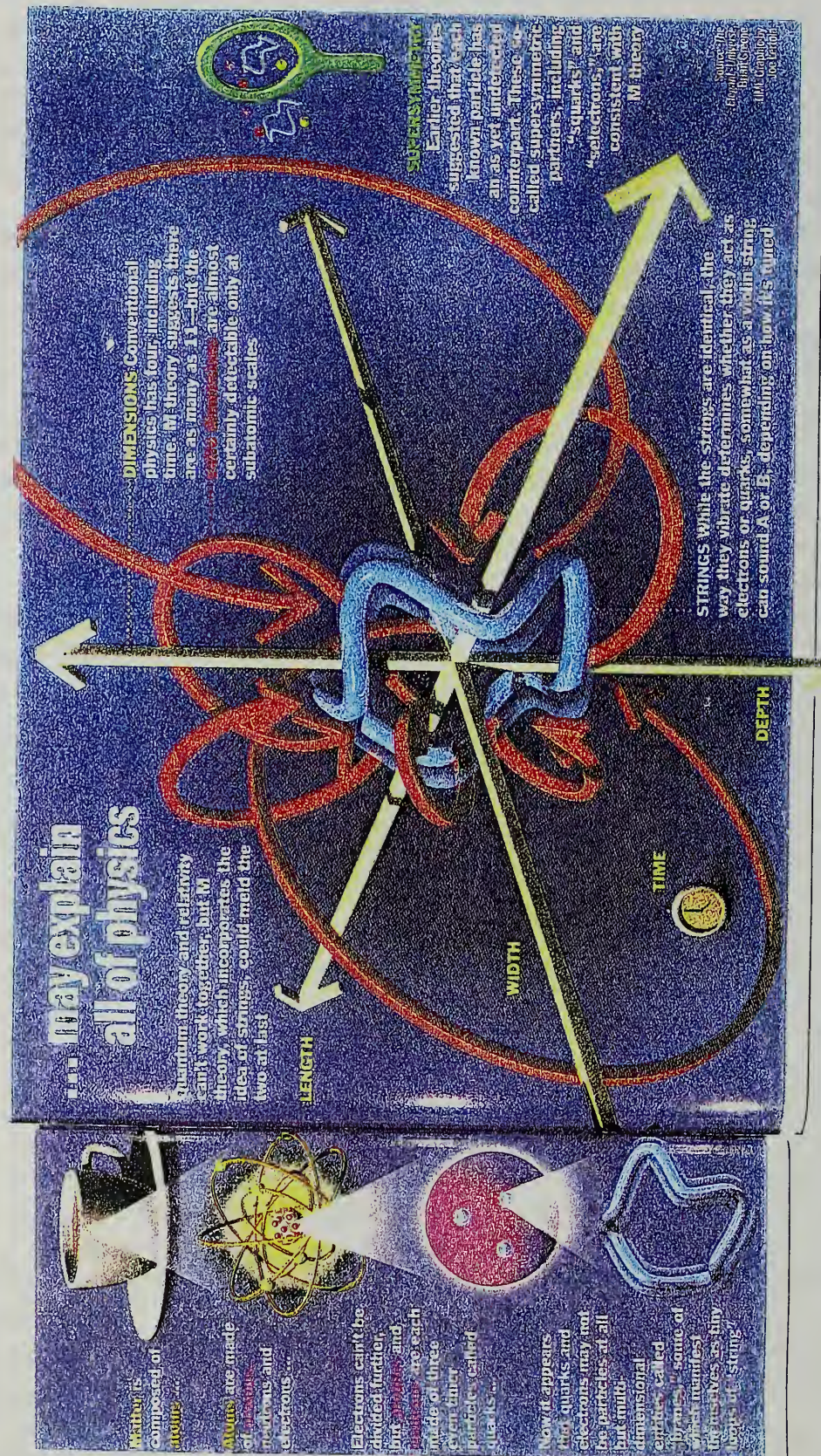


Figure 1. M theory (an offspring of chaos and complexity theory) suggests there are as many as 11 dimensions, but the extra dimensions are detectable only at subatomic scales. Quantum theory and relativity can't work together, but M theory, which incorporates the idea of strings, could meld the two at last [46].

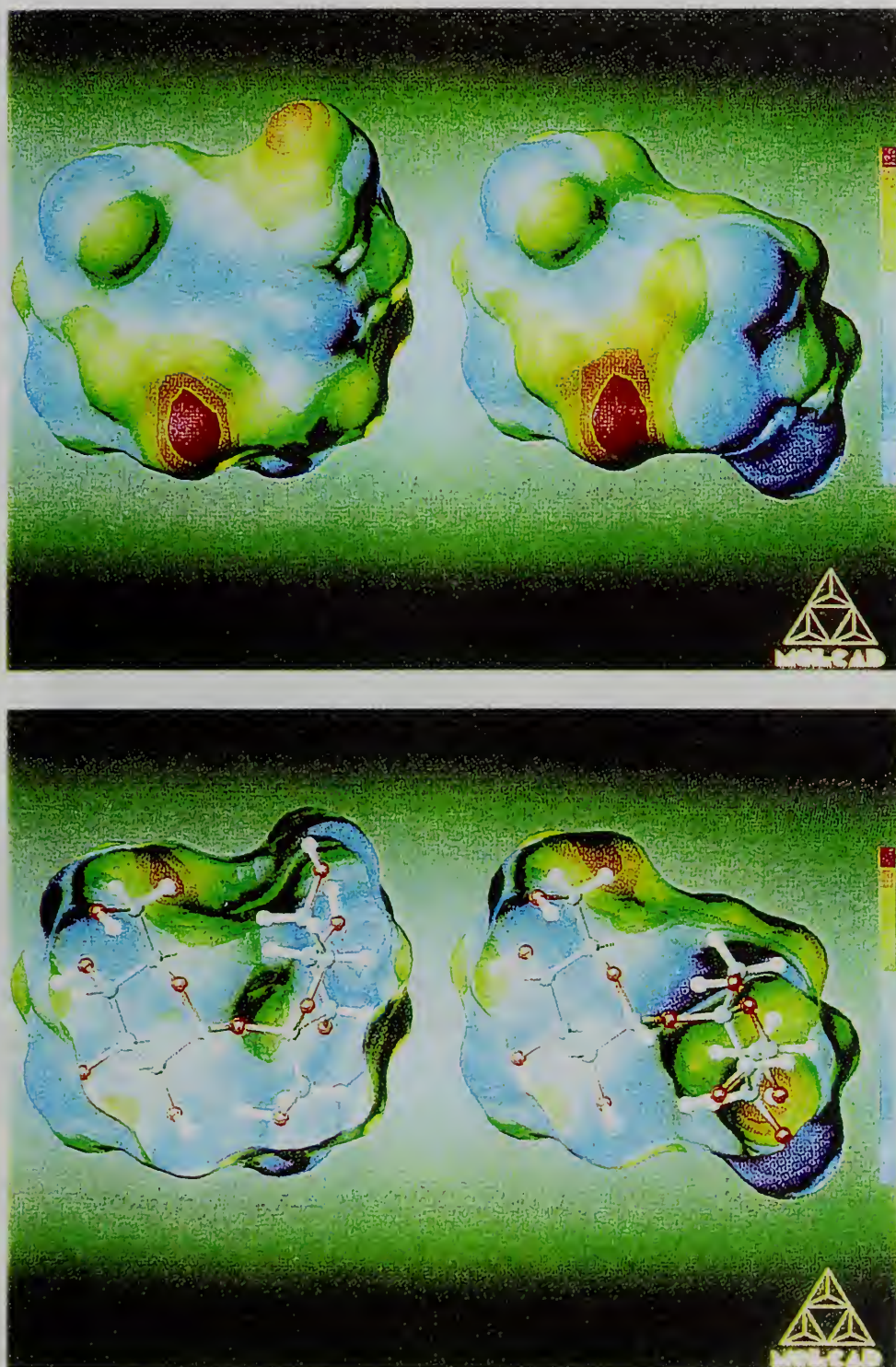


Figure 2. Representation of the molecular electrostatic potential (MEP) profiles of the two relevant sucrose conformers emerge from PIMM88 calculations (cf. Figure8). The MEP's are depicted on the corresponding contact surfaces in a 16-color code ranging from violet (most negative potential) to red (most electropositive potential) in relative terms. To facilitate visualization, the front side-opened forms of the two conformers are also provided with a ball-stick model inserted. In either case, it is evident that the proton of the 2-OH group of the glucose part is characterized by a high positive electrostatic potential (red), indicating its enhanced acidity over other OH protons [18]. (Lichtenthaler, 1994)

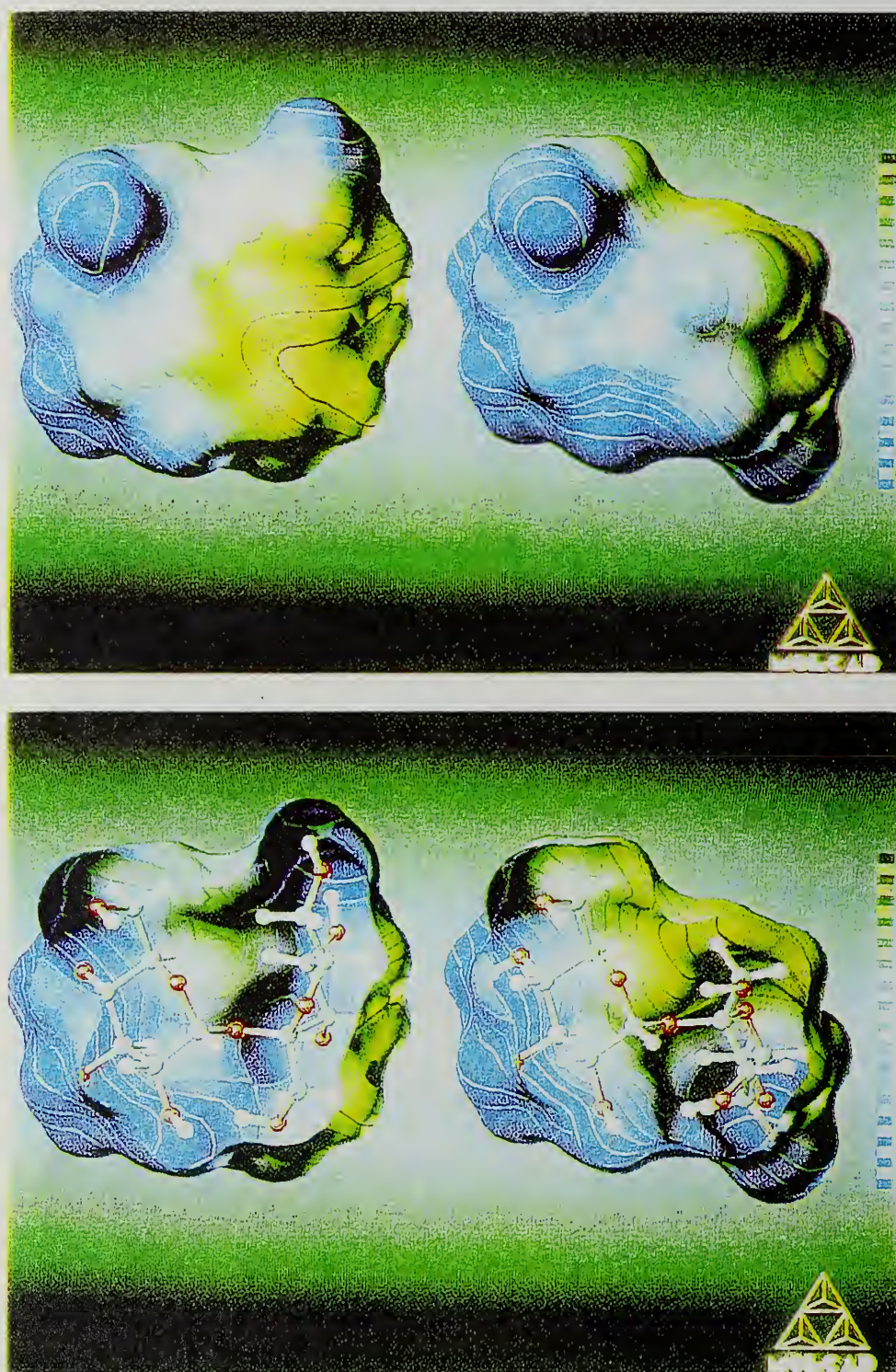


Figure 3. Molecular lipophilicity profiles for the two sucrose conformers of Figure 8, blue corresponding to hydrophilic surface areas and yellow to most hydrophobic regions. For both sucrose conformers, the entire “backside” of the fructose moiety is decisively hydrophobic [18]. (Lichtenthaler, 1994)



Figure 4. Various sucrose crystal forms viewed by polarized light. The colored micrographs are a selection from the large collection of extremely varied forms in which sucrose will crystallize under humidity control. (a) Originates as a spherulite. (b) Originates from a normal polyhedral crystal. (c) A filamentous form showing rhythmic weaving. (d) Exhibiting various forms of rhythmic growth. When seen by time-lapse film, the rhythmic growth often pulses in a manner reminiscent of heart beats [47].

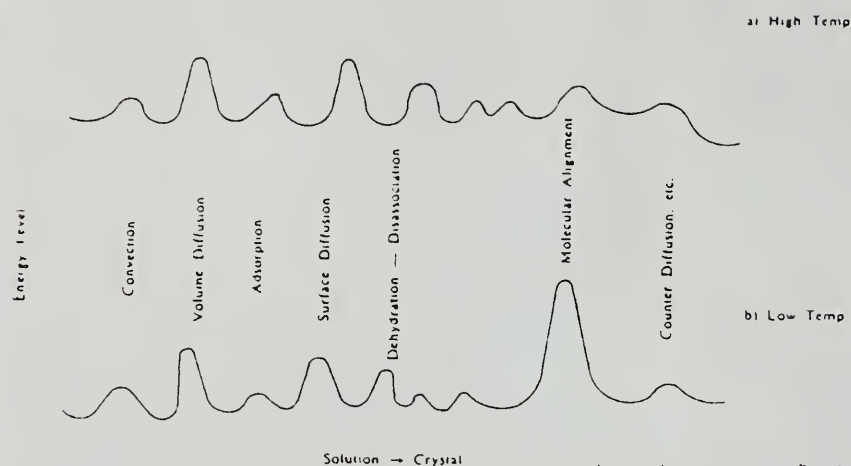


Fig. 3 Possible course of sugar crystallization.

Van Hook 1981 [52] Fig. 5b



spiral shape on the a (100) (Dunning 1967) face of a sucrose crystal grown in pure solution [30] Fig. 5a

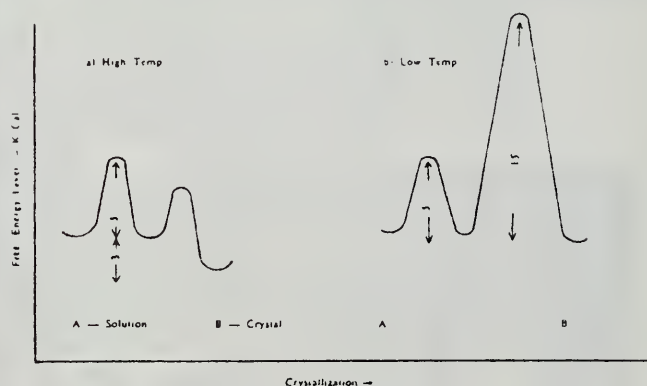


Fig. 2: Minimal reaction coordinate scheme of sugar crystallizations [30] Fig. 5c

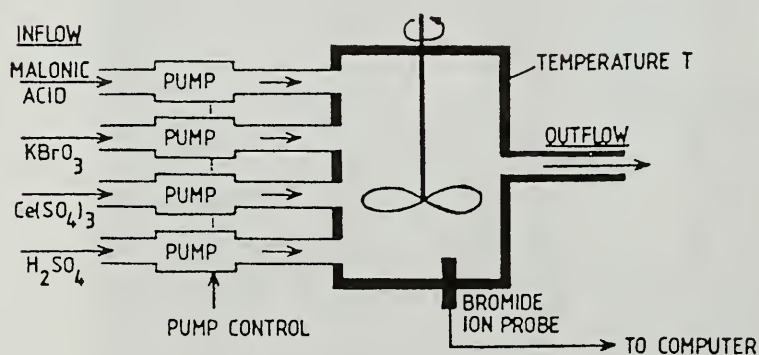


Fig. 5: Schematic representation of a chemical reactor used to study the oscillations in the Belousov-Zhabotinsky reaction (there is a stirring device in the reactor to keep the system homogeneous). The reaction has over thirty products and intermediates. The evolution of different reaction paths depends (among other factors) on the entries controlled by the pumps. [31] Fig. 5d

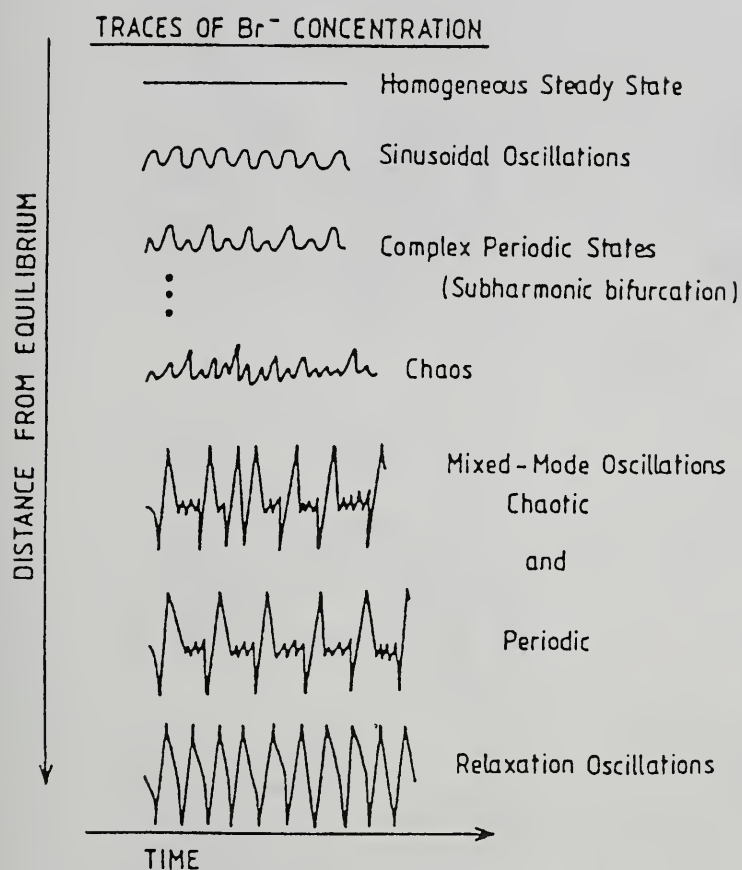


Fig. 6: Temporal oscillations of the Br^- ion in the *Belousov-Zhabotinski* reaction. The Figure represents a succession of regions corresponding to qualitative differences. This is a schematic representation. The experimental data indicate the existence of much more complicated sequences. [31, 32, 33]

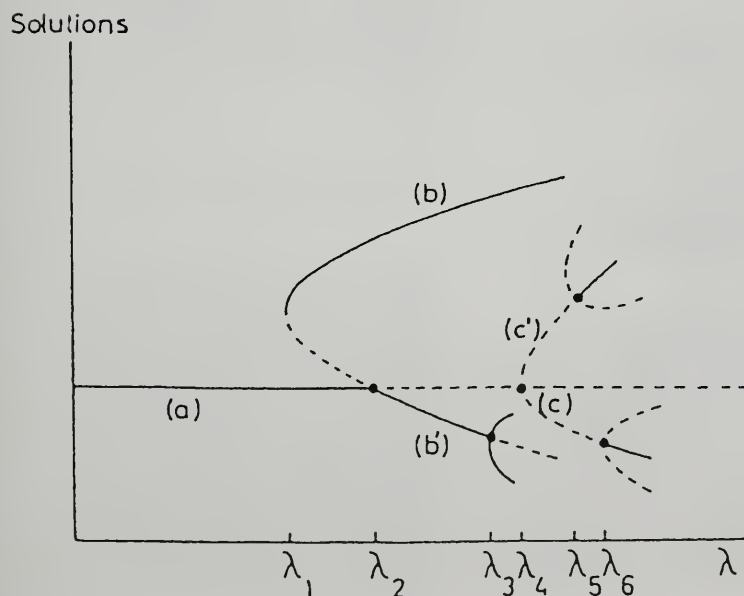


Fig. 7: Bifurcation diagram. Steady-state solutions are plotted against bifurcation parameter λ . For $\lambda < \lambda_1$, there is only one stationary state for each value of λ ; this set of states forms the branch (a). For $\lambda = \lambda_1$, two other sets of stationary states become possible [branches (b) and (b')]. The states of (b') are unstable but become stable at $\lambda = \lambda_2$ while the states of branch (a) become unstable. For $\lambda = \lambda_3$, the branch (b') is unstable again, and two other stable branches appear. For $\lambda = \lambda_4$, the unstable branch (a) attains a new bifurcation point where two new branches become possible, which will be unstable up to $\lambda = \lambda_5$, and $\lambda = \lambda_6$. [31, 32, 33]

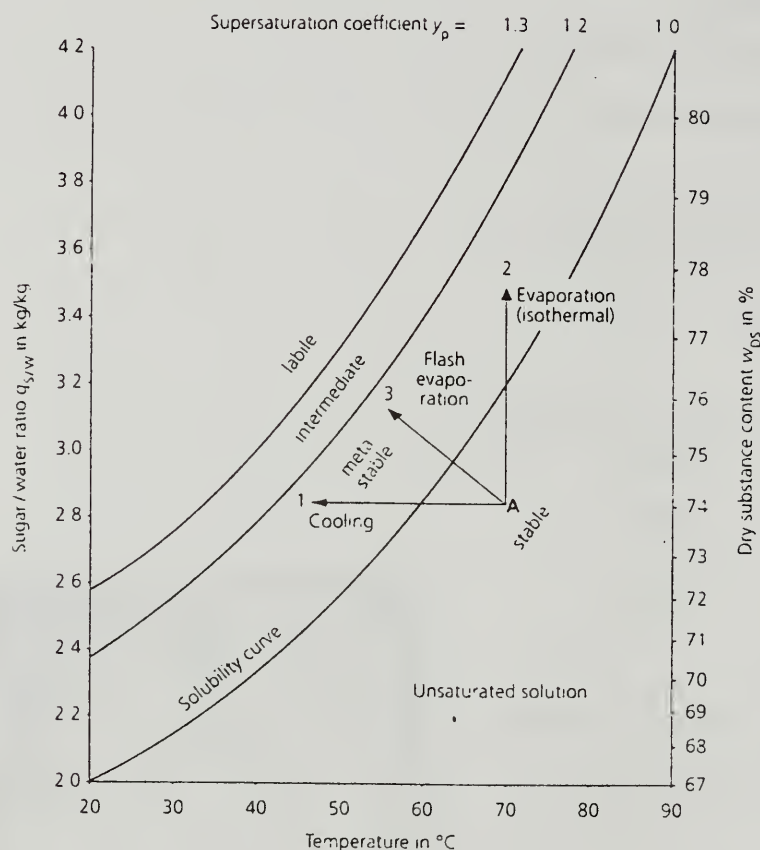
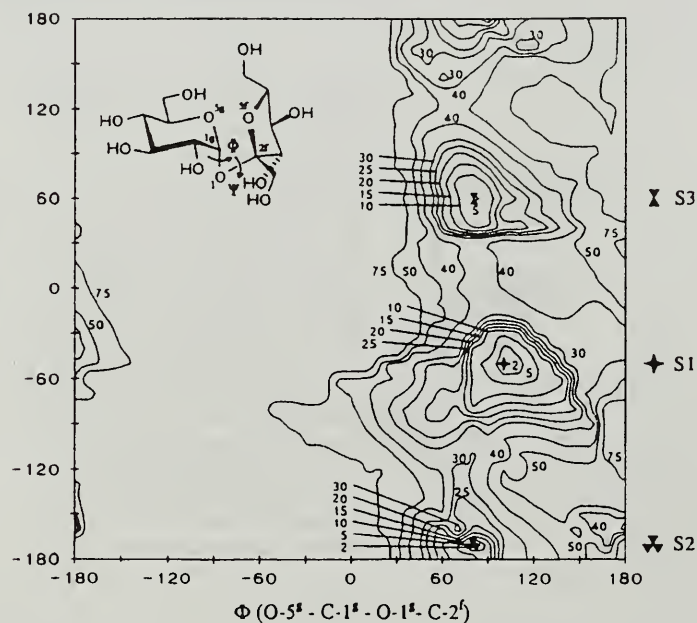


Figure 12 : Dry substance content and sugar/water ratio of pure saturated ($y_p = 1$) and supersaturated ($y_p = 1.20$, $y_p = 1.30$) sucrose solutions as a function of temperature [27a]

Ψ (C-1^s - O-1^s - C-2^f - O-5^f)



Lichtenthaler 1995

Fig. 8: Fully, relaxed energy potential surface of sucrose as a function of the intersaccharide torsion angles Φ and Ψ , corresponding to the rotation about the C-1^s-O-1^s (Φ) and O-1^s-C-2^f (Ψ) bonds, respectively. Energy contours are given in kJ/mol relative to the global minimum at $\Phi \approx \pm 110^\circ$ (designated as S1). The molecular geometry for S1 (cf. ball-and-stick models of Fig. 9) closely conforms with the conformation depicted in 1e, that of S2 with formula 1f. [1b]

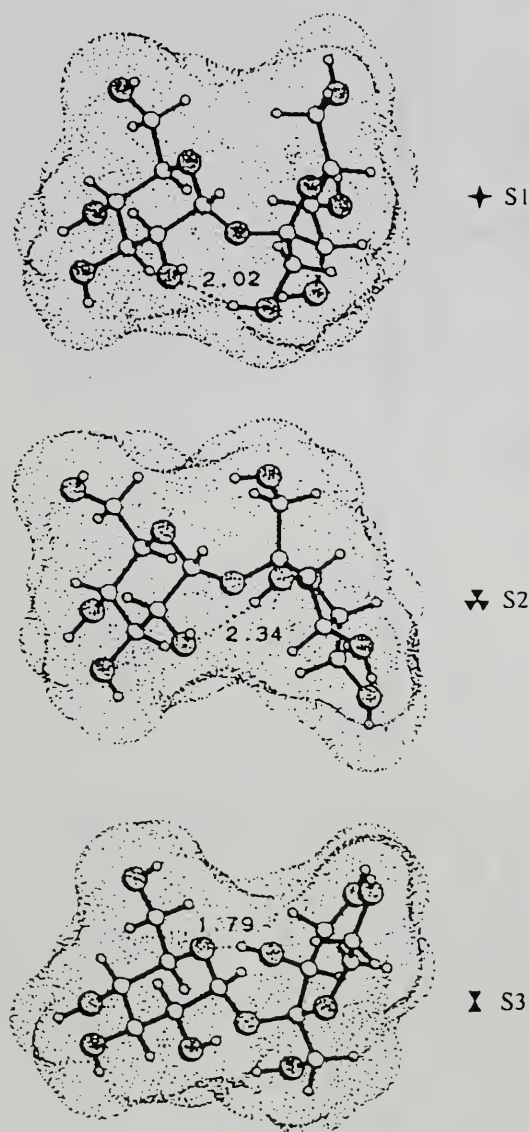
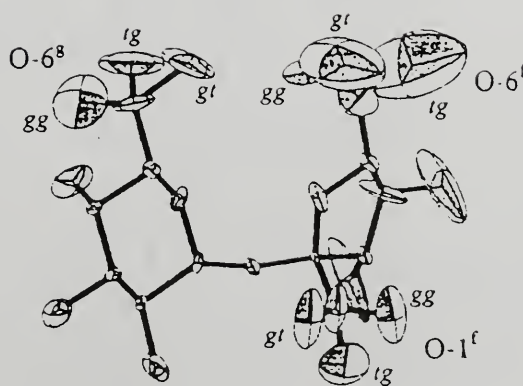
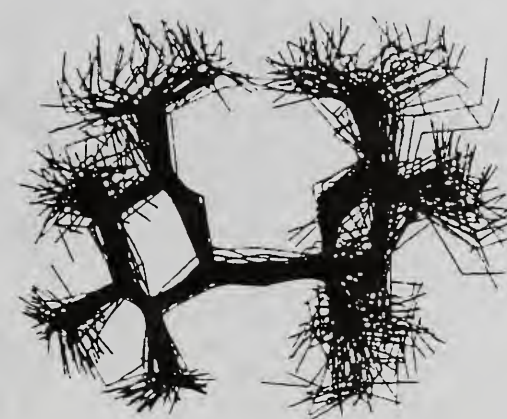


Fig. 9: Ball-and-stick model representation, also comprising the contact surface in dotted form, of the three low-energy conformers (S1–S3) of sucrose that emerge from the PLMM88 force-field calculations of Fig. 8. The major conformer S1 displays intersaccharidic torsion angles Φ and Ψ close to those observed in the crystal; its overall molecular geometry comprising the $2^f\text{-O}\cdots\text{HO-1}^f$ inter-residue hydrogen bond resembles largely that implied by the conventional formula drawing [e. [15] 1.21].



Lichtenthaler, 1995

Fig. 10: Superimposition of 100 sucrose snapshot-geometries taken in 5 ps intervals from a 500 ps molecular dynamics simulation on an assembly comprising sucrose in a box of 571 water molecules. For clarity, hydrogen atoms and water molecules are omitted. Least-squares fitting was performed by rigid body translation and rotation of the molecules, considering only the tetrahydropyran-oxo-tetrahydrofuran backbone. In the lower plot, the atomic mean positions and anisotropic thermal probability ellipsoids at the σ -level as obtained from the MD are shown. The thermal ellipsoids for the three staggered arrangements for each of the hydroxymethyl groups (*gg*, *gt* and *tg* forms, respectively) are indicated separately; they signify their individual flexibility, not their relative populations, as adoption of the *gg* and *gt* forms is highly preferred. During the entire simulation only one transition of the glucose-6- CH_2OH to the *tg* conformation was observed. [67 1.91]

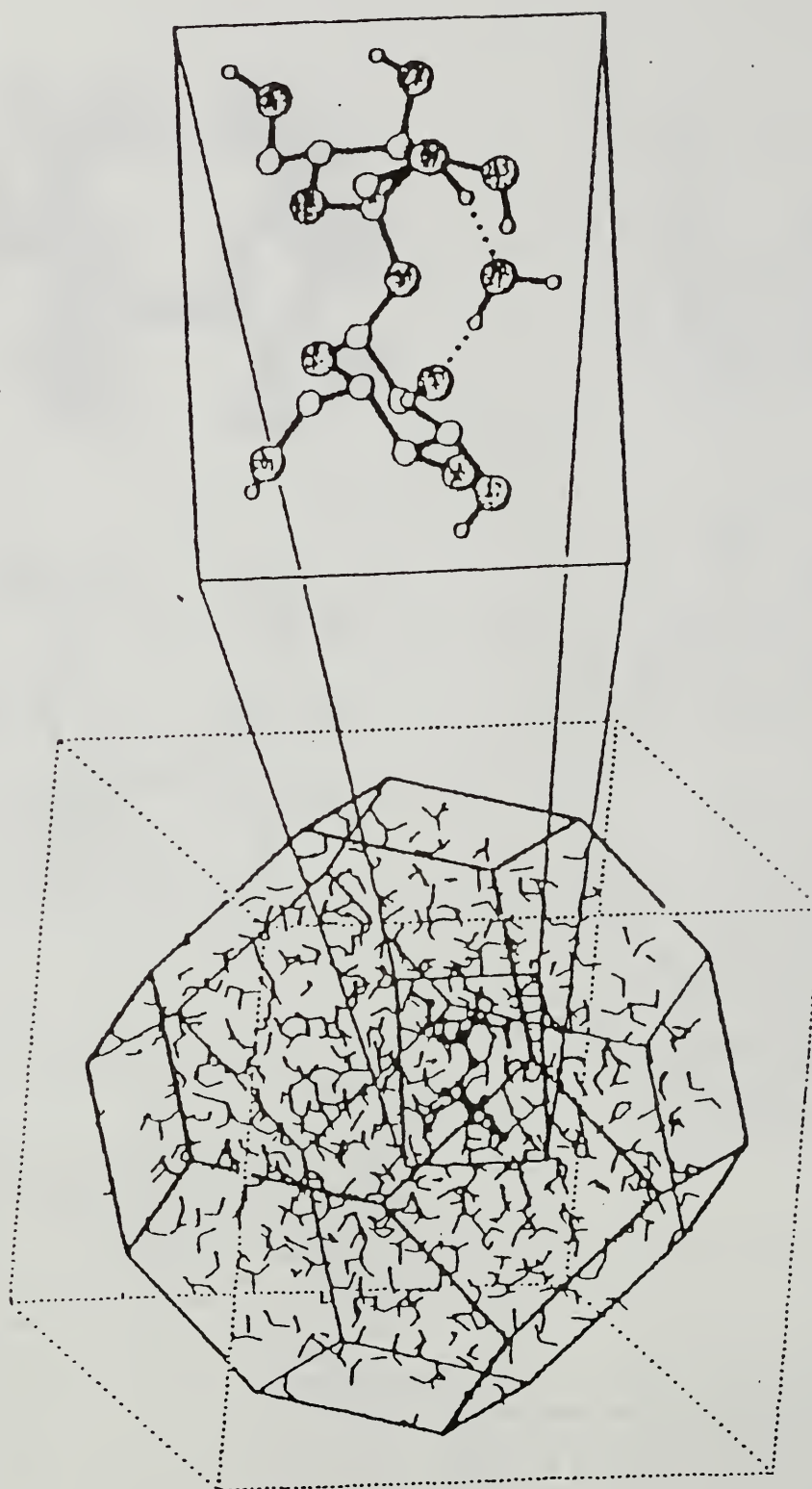


Figure 11. Snapshot of a MD simulation of sucrose surrounded by 571 water molecules (box-size of the truncated octahedron approximately 39.2 Å, volume ca. 17,800 Å³) with one water molecule hydrogen-bonded between 2^g - O and I^f - O [19] (Lichtenthaler & Immel, 1995)

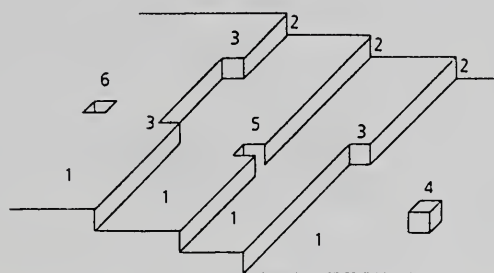


Figure 12/5: Kossel's model for crystal growth
1 Flat surface; 2 Steps; 3 Kinks; 4 Growth unit; 5 Edge vacancy; 6 Surface vacancy [39] (1998)

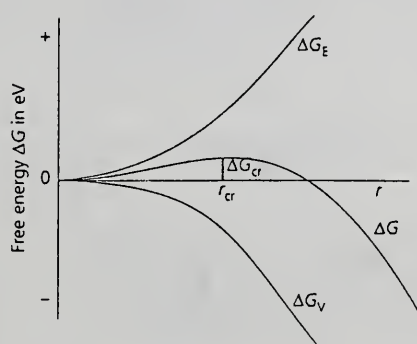


Figure 12/7: Free energy diagram for two-dimensional nucleation [39] (1998)

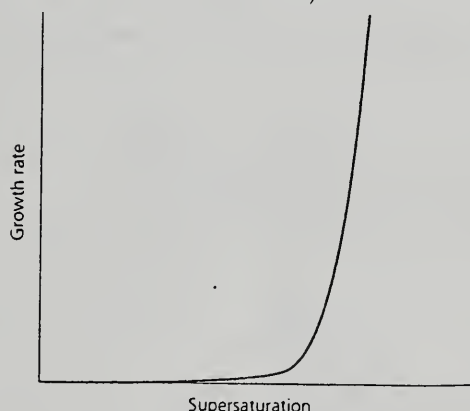


Figure 12/8: Growth rate isotherm according to two-dimensional nucleation mechanism [39] (1998)

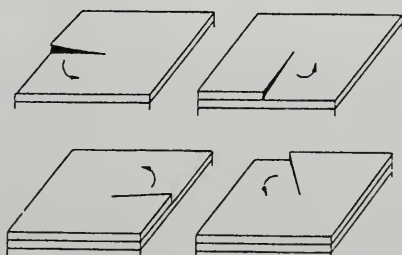


Figure 12/9: Spiral growth starting from a screw dislocation [39] (1998)

6.1.2.5 Effect of axial dispersion

Only in the ideal case does the extraction liquid pass by the cossettes in laminar flow. In reality, there is some turbulence which is superimposed on the desired direction of the material transport along the extraction route and is characterized by the axial dispersion coefficient $D_{ax,2}$. Superimposed on this micro-mixing of the liquid phase is a macro-mixing caused by the churning of the essentially uniformly moving cossettes and which, analogously to the behavior of the liquid, can be represented by an axial dispersion coefficient $D_{ax,1}$.

The solid phase and the liquid phase move against each other at defined velocities respectively. The mean cossette velocity is:

$$u_1 = \frac{\dot{V}_1}{\varepsilon_1 \cdot A_Q} \quad (6.27)$$

while the liquid (eq. 6.9) flows through the extractor at a mean velocity of:

$$u_2 = -\frac{\alpha_v \cdot \dot{V}_1}{\varepsilon_2 \cdot A_Q} \quad (6.28)$$

with ε_2 being related to ε_1 in accordance with equation (6.16). Determining the hydrodynamics of the liquid, however, is its flow through the spaces between cossettes. In this respect, it is useful to transform the countercurrent as an apparently resting phase on to the cossette phase. The difference velocity is:

$$u = u_1 \cdot \Phi_1 \quad (6.29)$$

with:

$$\Phi_1 = 1 + \alpha_v \cdot (\varepsilon_1 / \varepsilon_2) \quad (6.30)$$

Hence the extraction is described by the following partial differential equation:

$$\frac{\partial c_2}{\partial t} = \frac{\partial \bar{c}_1}{\partial t} + u \cdot \Phi_1 \cdot \frac{\partial \bar{c}_1}{\partial z} - D_{ax} \cdot \Phi_1^2 \cdot \frac{\partial^2 \bar{c}_1}{\partial z^2} \quad (6.31)$$

where \bar{c}_1 and c_2 respectively represent the sucrose concentration in the cossettes and in the liquid along the extraction route z , while D_{ax} is the axial dispersion coefficient comprising the effective contribution of macro- and micromixing ($D_{ax,1}$ or $D_{ax,2}$ respectively). During constant countercurrent operation, the principle of quasi-stationariness applies, i.e. the concentration at point z is independent of time:

$$\frac{\partial c_2}{\partial t} = 0 \quad (6.32)$$

Buttersack C. & Schüepfke [8], [39]
(1998)

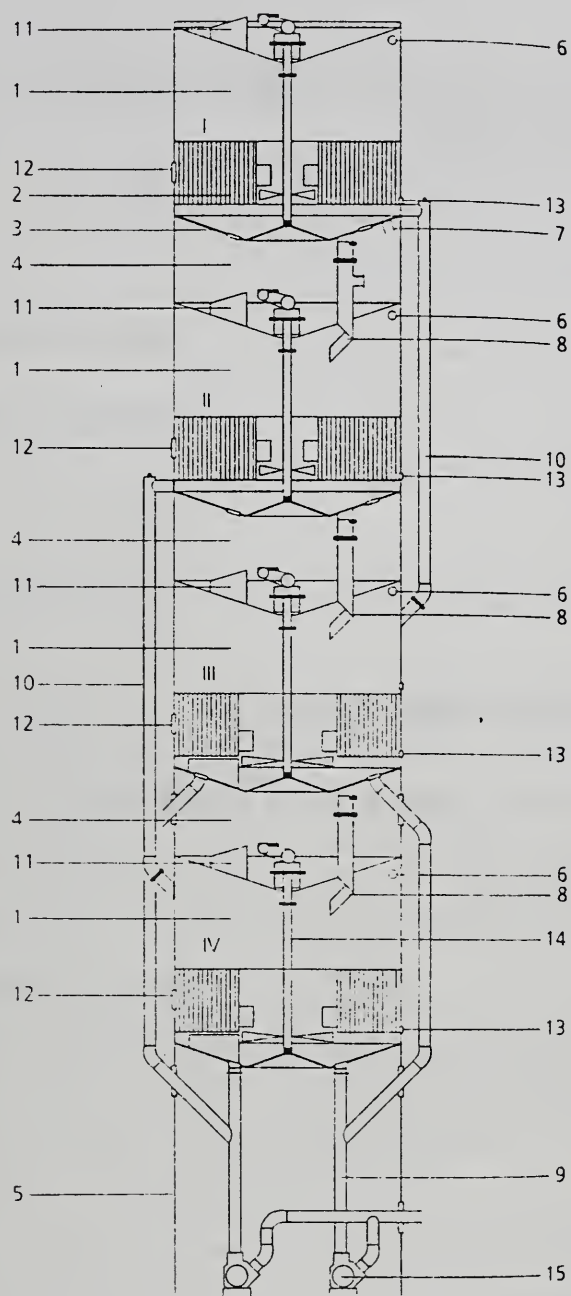


Figure 12/143: VKT for crystallization of white sugar
 1 – IV Crystallizing chambers; 1 Vapor space; 2 Calandria; 3 Drain plate; 4 Intermediate section; 5 Support section; 6 Feed syrup inlet; 7 Seed magma inlet; 8 Magma transfer pipe; 9 Final magma outlet; 10 Bypass; 11 Crystallization vapors outlet; 12 Heating steam inlet; 13 Condensate outlet; 14 Stirrer; 15 Magma pump (+ standby pump)

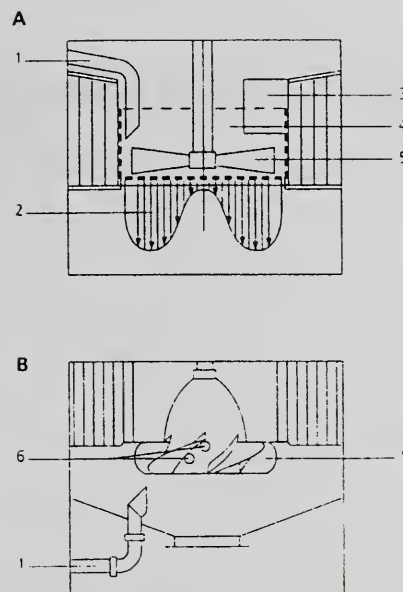


Figure 12/139: Position of paddle (A) and turbine (B) stirrers and syrup inlet in batch evaporating crystallizers
 1 Syrup feed pipe; 2 Turbulent flow pattern; 3 Radial counter blades; 4 Mixing chamber; 5 Stirrer; 6 Openings for syrup movement

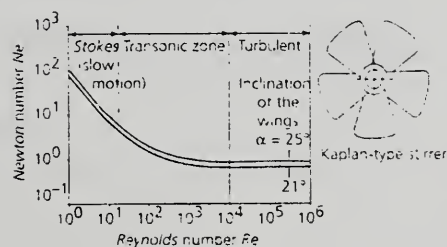


Figure 12/140: Power characteristics for a Kaplan-type 5-bladed stirrer (Austmeyer 1986)

SPECIAL REVIEW SECTION
LITERATURE SURVEY ON MOLASSES EXHAUSTION

Martine Decloux

LITERATURE SURVEY ON MOLASSES EXHAUSTION

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INTRODUCTION

The objective of this report is to present a summary of the work conducted on molasses exhaustion in the literature with the goal to study if it is possible to increase molasses exhaustion by altering the non-sucrose content before cooling crystallization. Furthermore, our objective is to compare and understand the differences between beet and cane molasses.

The molasses exhaustion is not the point from which no more sugar can be crystallized, but rather the point from which no more appreciable amounts of sugar can be economically recovered. Nevertheless, sucrose solubility in molasses is one of the important parameters to consider.

Sucrose is highly soluble in water. Pure sucrose solubility is related to temperature as :

$$DS_{\text{saturation}} = a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 + a_4 \cdot T^4 \quad DS: \% \text{ dry solids, } T \text{ in } ^\circ\text{C}$$

Some correlations are reported in **Table 1**.

Table 1. Pure sucrose solubility equations

Authors	a_0	a_1	a_2	a_3	a_4
Liang (1988)	62.770	0.17060	$0.3440 \cdot 10^{-3}$		
Peacock (1995)	63.735	0.14189	$0.5635 \cdot 10^{-3}$		
Charles (McGinnis 1978)	64.397	0.07251	$2.5690 \cdot 10^{-3}$	$9.035 \cdot 10^{-6}$	
Vavrinecz (McGinnis 1978)	64.447	0.08222	$1.6617 \cdot 10^{-3}$	$1.558 \cdot 10^{-6}$	$-4.63 \cdot 10^{-8}$
Peacock (1995)	63.753	0.13542	$0.8869 \cdot 10^{-3}$	$-2.222 \cdot 10^{-6}$	

Sucrose solubility does not vary in the same way in beet and cane impure solutions. According to Grut's table modified by Bubnik and Kadlec (van der Poel *et al.* 1998) for beet syrups and Thieme's table (Hugot 1972) for cane syrups, it can be seen (**Figure 1a**) that sucrose solubility decreases regularly as the purity decreases in cane solution, whereas it increases in low purity beet solutions (purity lower than 85). Thus, dry solids at saturation increases slightly in cane solutions whereas it increases sharply in beet solutions (**Figure 1b**). Furthermore, in each category, beet and cane, differences in sucrose solubility are observed among the different countries.

The influence of non-sucrose on sucrose solubility is generally characterized as a ratio of sucrose solubility in impure solution to sucrose solubility in pure sucrose solution at the same temperature. This ratio is known as the solubility coefficient (SC) :

$$SC = \left[\frac{\left(\frac{S}{W} \right)_{\text{impure solution}}}{\left(\frac{S}{W} \right)_{\text{pure solution}}} \right]_T$$

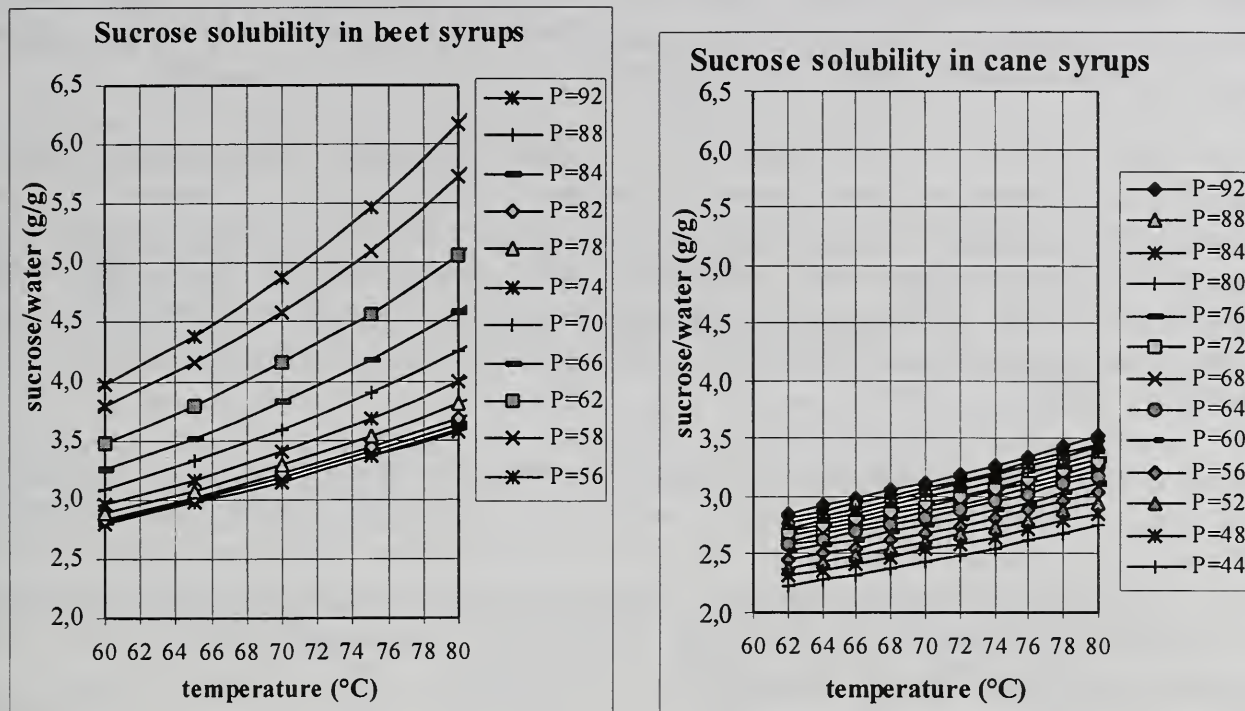


Fig.1a : Sucrose solubility in beet (Grut's table) and cane (Thieme's table) impure solutions

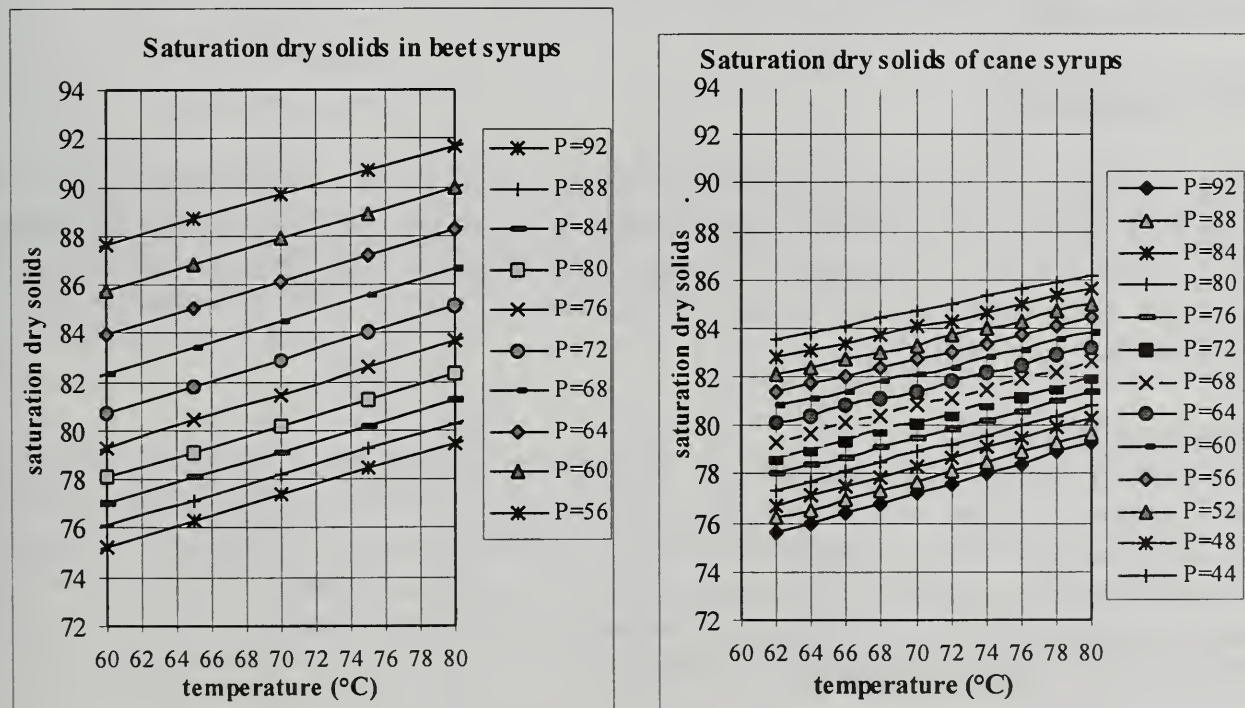


Fig.1b : Dry solids at saturation in beet and cane solutions

The methods used to determine the sucrose solubility can be classified according Wright (1980) into two distinct groups :

1. Those which seek to use a selected property of a seeded syrup which changes significantly when a small degree of undersaturation is reached (usually by controlled heating). A great deal of research has been done to find a suitable property of seeded syrup sample.
2. Those which rely on the equilibration of the syrup with excess crystal sucrose under conditions of agitation at a set constant temperature, followed by the separation and the analysis of the equilibrated mother liquor as a comparison with the original syrup analysis. This method may be used with unsaturated syrup (Polish test) or more often with supersaturated syrup. In that case, the method to measure the sucrose solubility is very similar to a molasses exhaustibility test. The duration of the test is the main factor which may differentiate them.

Results on molasses exhaustion tests may differ significantly according to the molasses category, beet and cane, and to the analytical methods used to characterize the products (solids, sucrose, non-sucrose, ash, viscosity). Thus, in the first part of this literature survey we report data on molasses composition and analytical methods. Then in the second part, we present the studies on sucrose solubility in molasses and on molasses exhaustibility altogether as these are two very linked notions which are difficult to distinguish.

1. BACKGROUND

1.1 APPROXIMATE COMPOSITION OF MOLASSES

1.1.1 Beet molasses

According to McGinnins (1982), a typical approximate analysis of beet molasses is 81-84% solids, 50-52% sucrose, 21-31% organic compounds (nitrogenous 12-13% and non nitrogenous 9-10%), 11-12% ash and 2% inorganic nitrogen. Typical values from literature are shown in **Table 2** and average compositions of French beet molasses from seven factories during the 91-92 season are shown in **Table 3**.

Non sucrose carbohydrates :

These consist of invert sugar, usually less than 1% in straight house molasses, raffinose, galactinol, inositol, kestose and possibly others. Invert sugar is never found in beet molasses in amounts large enough to have an appreciable effect on molasses purity. The raffinose content of beet molasses exerts a measurable lowering effect on sucrose solubility, but its potential lowering of molasses purity is not obtained in practice because of the marked reduction in rate of crystallization of sucrose in the presence of raffinose.

Organic non sugars :

- Nitrogenous compounds. Betaine (a nitrogenous base) is the most abundant nitrogenous compound found in beet molasses. It increases toward the end of the campaign. The second most abundant nitrogen compound is glutamine and its hydrolytic products, pyroglutamic acid and glutamic acid. This group constitutes more than half of the total amino acids content of molasses. Inorganic nitrogen, i.e. nitrogen as nitrates and nitrites occur in amounts ranging from near traces to 5% or more of the nitrogen in beets.

- Non nitrogenous acids : lactic, malic, acetic, oxalic, citric and others formed in part by bacterial action or by destruction of invert in the clarification process. D-, L-lactic acid content is approximately one third of the total organic anions. Lactic acid is formed by alkaline invert sugar destruction during juice purification and/or via microbiological activity during juice extraction (Schiweck 1994).

Ash : Potassium (K^+) and sodium (Na^+) are the most abundant ions. Calcium and magnesium are normal constituents of beets, but only about 10% of the calcium and 50% of the magnesium is extracted in diffusion and almost all of the magnesium is ultimately eliminated in carbonation as well as the calcium except when processing deteriorated beets. Even if calcium, and particularly magnesium, tend to decrease sucrose solubility, their concentration in molasses is usually so low compared to potassium and sodium that they do not materially affect the ratio of sucrose to ($K^+ + Na^+$). This last ratio, known as the Winklund ratio, is particularly important in molasses exhaustibility as illustrated later on.

Table 2. Average composition of beet molasses and comparison with cane molasses

	McGinnis 1982	Ramm- Schmidt 1988	Schiweck 1994	quoted by McGinnis 78 from Olbrich 1956	
Constituents	Beet (%)	Beet (%)	Beet (%)	Beet (%)	Cane (%)
Total solids	81-84	80	> 76	84.5	80.0
Water				16.5	20.0
Sugars				53.0	62.0
- Sucrose	50-52	53.2	47	51.0	32.0
- Glucose				-	14.0
- Fructose				-	16.0
- Invert sugar		1.2	0.1-0.5	1.0	
- Raffinose		1.2	0.3-1.5	1.0	-
Organic Non-Sugars	21-31	18.4	19	19.0	10.0
- nitrogenous materials	12-13	10.0	12		
free and bounds acids	9-10	4.4	7		
soluble gummy subs.		4.0			
Ash	11-12	8.4	10	11.5	8.0
- SiO_2		0.08		0.1	0.5
- K_2O		4.8		3.9	3.5
- CaO		0.16		0.26	1.5
- MgO		0.16		0.16	0.1
- P_2O_5		0.08		0.06	0.2
- Na_2O		0.8		1.3	
- Fe_2O_3		0.08		0.02	0.2
- Al_2O_3				0.07	
- sulfates residues (as SO_3)		0.4		0.55	1.6
- Chlorides		1.4		1.6	0.4
Inorganic nitrogen	2				

Table 3. Average French **beet molasses** composition during the 1991-92 campaign (UCB data)

Factory	1	2	3	4	5	6	7	ave
Total solids (refractometer)	79.73	80.95	81.80	75.50	79.73	79.93	77.35	79.28
Sucrose (%molasses)	50.24	49.93	49.77	55.33	49.06	46.64	53.23	50.60
Purity	63.0	61.7	60.8	73.3	61.5	58.4	68.8	63.9
pH	8.7	7.6	8.8	8.3	7.7	8.8	9.6	8.5
Col (IU)	42,518	49,043	45,599	34,172	37,125	44,289	29,994	40,291
Reducing sugars (%solids)	0.0076	0.0198	0.0012	0.0090	0.0272	0.0135	0.0021	0.0115
Raffinose (%solids)	2.36	2.30	2.50	1.35	2.29	2.14	1.77	2.10
Nitrogenous (%solids)	2.23	2.29	2.00	1.42	2.46	2.53	1.71	2.09
Sulphated ash (%solids)	11.89	12.38	14.32	9.34	11.60	13.16	11.82	12.07
K ⁺ (%solids)	4.77	4.69	5.75	3.52	3.96	4.67	4.29	4.52
Na ⁺ (%solids)	0.44	0.67	0.43	0.50	0.71	1.10	0.81	0.67
Ca ²⁺ (%solids)	0.05	0.10	0.23	0.03	0.18	0.08	0.03	0.10
Non-sucrose/Ash	3.11	3.09	2.74	2.86	3.32	3.16	2.64	2.99

1.1.2 Cane molasses

As noted by Chen and Chou (1993), a typical analysis cannot be formulated for cane molasses, but certain general figures are available (**Table 4**).

The broad range of cane molasses as it comes from the centrifugals would be 85-92 Brix or about 77-84% solids by vacuum drying. The sucrose varies between 25 and 40%, and the reducing sugars from 5 to 12%, with the sum of the two (total sugars) 50% or more. Ash in blackstrap molasses shows more than 10 or 11%, and 12-15% is quite common. Figures as high as 25% have been reported for molasses from South America (Saska 1999). Almost all analyses show potash ranging around 40% of the total carbonate ash, lime is next varying from 10-20%, sulfates are usually third varying from 10 to 20%, and magnesium salts, silica, chlorides, phosphate, sodium, aluminium, and iron oxides making the rest.

More precise composition of molasses during the 1999 season in two Louisiana cane mills was given by Iqbal and Andrews (2000) in **Table 5**. It can be seen that the reducing sugars (glucose + fructose) to ash ratio (RS/Ash) is in the range of 0.9-2.7 with a decreasing tendency as the season progresses. A similar tendency has been observed by Smith (1995) in four South African factories but the range was much lower (0.4 to 1.4). Non-sucrose to water ratios (NS/W) vary from 1.4 to 3.34. Nevertheless, this value may not correspond to the one just at the end of the cooling crystallization, as water may be introduced in the centrifugals. Cations represent nearly 40% of the ash. The most important cations are potassium and calcium. Magnesium and sodium are in low concentrations. These results agree with the ones obtained by Sahadeo (1998) in various mills during the 1996 crushing season in South Africa (**Table 6**).

Table 4. Approximate composition of **cane molasses** (Chen and Chou 1993)

	Normal %	Range
Total solids (vacuum drying is assumed)	83	-75
Water	17	- 25
- Sucrose	30	- 40
- Glucose	4	- 9
- Fructose	5	- 12
- Other reducing substances	1	- 4
Total reducing substances (as invert)	10	- 25
Organic Non sugars	8.4	- 21.5
- Nitrogenous Compounds		
- crude protein (N*6.25)	2.5	- 4.5
- true digestible protein	0.5	- 1.5
- amino acids : principally aspartic and glutamic	0.3	- 0.5
- unidentified nitrogenous compounds	1.5	- 3.0
- Non Nitrogenous acids :		
- aconitic acid (1-5%), citric, malic, oxalic, glycolic	1.5	- 6.0
- mesaconic, succinic, fumaric, tartaric	0.1	- 1.0
- other Carbohydrates (gums, starch, pentosans, traces of hexitols and uronic acids)	2	- 5
- Wax, sterols and lipids	< 1	
- Vitamins	< 1	
Ash (as carbonate)	7	- 15
Percent of Ash		
- K ₂ O (potash)	30-50	
- CaO (lime)	7-15	
- MgO	2-14	
- Na ₂ O	0.3-9	
- R ₂ O ₃ (Fe)	0.4-2.7	
- SO ₄ (sulfates)	7-27	
- Cl (chlorides)	12-20	
- P ₂ O ₅ (phosphates)	0.5-2.5	
* SiO ₂ and insolubles	1-7	
<i>Non Sucrose/water</i>	<i>1.4</i>	<i>-3.11</i>

Table 5. Composition of final **cane molasses** during 1999 season (Iqbal and Andrews 2000) [Solids (dilution 1:1 and refractometry) ; sucrose (HPLC) ; invert (HPIC) ; ash (conductivity) ; cations (HPIC) ; color (IU) ; turbidity (IU) ; total polysaccharides by SPRI method]

	Early season			mid season			end
Sample	1	2	3	4	5	6	7
Total solids (refractometer)	85.3	78.4	83.6	82.8	81.2	81.8	80.4
Water (water%molasses)	14.7	21.4	16.4	17.2	18.8	18.2	19.6
Sucrose (%solids)	42.4		38.	42.8	44.4	40.6	47.8
NS (non-sucrose%molasses)	49.1	53.9	51.5	47.6	45.2	48.6	42.0
NS/W (non-sucrose/water)	3.34	2.50	3.14	2.77	2.4	2.67	2.14
glucose + fructose (%solids)	22.96	17.15	24.42	29.66	12.00	14.24	12.16
Ash (%solids)	10.97	11.87	11.87	11.08	13.42	13.03	13.34
Reducing sugars/Ash	2.1	1.4	2.0	2.7	0.9	1.1	0.9
Na ⁺ (%solids)	0.03	0.03	0.63	0.07	0.04		0.07
K ⁺ (%solids)	2.94	3.34	2.83	2.98	2.32		3.85
Mg ⁺⁺ (%solids)	0.45	0.51	0.44	0.46	0.63		
Ca ⁺⁺ (%solids)	0.90	0.91	0.90	1.23	1.18		
Total cations (%solids)	4.33	4.88	4.81	4.74	4.18		
pH	6.3	5.9	5.6	6.1	5.8	6.0	6.1
color (IU)	71,469	70,330	91,500	87,750	113,000	94,400	85,500
turbidity (IU)	29,670	28,000	41,170	46,750	69,670	52,800	39,500
polysaccharides (%solids)	2.06	2.30	2.10	2.78	2.33	2.52	2.11

Table 6. Components of **cane molasses** from South Africa (Sahadeo 1998)

	(%)	(%solids)
Solids by vacuum oven	78.4	
Sucrose by gas chromatography	31.9	40.7
Glucose by GC	5.7	7.27
Fructose by GC	7.6	9.69
G+F	13.3	16.96
Organics non sugars	18.5	23.60
Sulphated ash	12.7	16.20
(F+G)/Ash	1.05	1.05
Na ⁺	0.09	0.11
K ⁺	2.96	3.77
Mg ⁺⁺	0.33	0.42
Ca ⁺⁺	0.83	1.06
gums	1.62	2.07
starch	0.007	0.009

Vercellotti, *et al.*, (1996) analyzed molasses during the 1995 season in cane mills of Louisiana and Florida (**Table 7**). The composition of cane refinery molasses (**Table 8**) shows about the same proportion of solids (44% sucrose, 18% reducing sugars, 12% ash and 12% organic non-sucrose).

Table 7. Components of **cane molasses** (Vercellotti et al. 1996)

	Louisiana (12 samples)		Florida (8 daily composite samples)	
	Average	Std. devia	Average	Std devia
Total solids (refractometer)	82.64	2.13	79.8	2.00
Vacuum solids	79.96	1.78	76.46	2.43
Pol degree	38.51	2.27	33.84	1.66
Apparent purity	46.63	3.15	42.40	1.47
Sucrose (%solids)	44.59	10.49		
Glucose (%solids)	3.38	1.16		
Fructose (%solids)	6.82	1.67		
F+G (%solids)	10.20	2.16		
Na ⁺ (%solids)	0.69	0.19		
K ⁺ (%solids)	3.78	7.54		
pH	5.98	0.19	6.09	0.05

Table 8. Components of cane molasses from a French refinery (Personal communication)

	%
Total solids (refractometer)	81.0
Sucrose by pol (%solids)	44.6
Reducing sugars (%solids)	18.4
Ash (%solids)	12.3
Organics non sugars (%solids)	24.7

1.1.3 Comparison of beet and cane molasses compositions

Concerning the sugars content, the reducing sugars may represent more than 10% solids in cane molasses, whereas it is lower than 0.1% in beet molasses. By contrast, beet molasses contains more sucrose and a high concentration of raffinose which reduces the sucrose crystallization rate.

Concentration of organic non-sucrose in beet molasses is more important (19% against 10% in cane molasses) and beet molasses contains a significant quantity of betaine and amino acids. The level of polysaccharides in cane molasses is in the range 2-2.5% and may constitute an important factor, but the literature is silent on this.

Average concentration of ash is in the same range for both beet molasses (11.5%) and cane molasses (10-15%). In both molasses, potassium is the main cation then sodium in beet molasses and calcium in cane molasses.

All these figures depend on the analytical methods used for their determination. As molasses is the least pure product of the sugar factory, analytical methods valuable for pure sucrose solutions may give incorrect values with molasses, and this problem may induce wrong interpretations afterwards. This aspect is discussed in the next section.

1.2 INFLUENCE OF ANALYTICAL METHODS ON MOLASSES ANALYSIS

1.2.1 Total solids

Even if the determination of solids seems a very simple analysis it is not the case for molasses. Several methods are referenced in the ICUMSA book methods :

- True percentage is supposed to be determined by vacuum oven drying on sand (ICUMSA Method GS4/7-11). The mass loss of molasses mixed with sand is determined following drying at 65°C in a vacuum oven with an absolute pressure not exceeding 6.7 kPa (1 psi) or a vacuum higher than 28 in hg (inch of mercury) for more than 18 hours.
- Brix by hydrometer (ICUMSA Method GS4-15) is the least precise method. It depends a lot on the dilution: the brix of a solution is different from the calculated one at another dilution. The difference is due partly to the contraction of the sugar solution on dilution with water and partly to a similar contraction of the solution of the salts in the molasses.
- Refractometric dry substance (RDS) (ICUMSA Method GS4-13) gives closer value to true dry substance than the figure obtained by hydrometer but always gives higher value (see later). In addition, dilution of concentrated solutions induces errors due to the volume contraction phenomenon (Schmidt and Moller 1964).
- the Karl Fisher method (ICUMSA Method GS4/7/3-12) yields values which are often up to 1 unit lower than the vacuum oven drying method (Ravno and Lionnet 1982).

Several studies have been performed to compare the different methods. True determination of solids content is important in this study on molasses exhaustion, since one of the most important parameters is the non-sucrose to water ratio (NS/W).

Recently, Vercellotti, *et al.*, (1998) compared solids contents in 6 samples (five molasses from different countries and a sugarbeet ion exclusion separator fraction rich in sucrose) using 3 methods:

1. Refractometer with a dilution (GS4-13)
2. Dynamic purge and trap drying method at 130°C for 25 min with helium at 40 mL/min (method proposed by Legendre and Fisher 1979 and 1981). This method gives very similar results to the ICUMSA one by vacuum oven drying on sand.
3. Thin film drying method: molasses sample (1 g) is spread in a thin film on the bottom or side of a tared 100 mL tall form beaker prior to final weighing. The sample is dried for 14 hours at 0.1 mm hg pressure (2 psi) at 50°C then during 10 hours at 90°C to constant weight.

Other compounds (invert, sucrose, high molecular weight compounds) were also measured before and after drying to check the influence of the drying on the composition.

Table 9 shows that refractometric method over-estimates real solids in molasses. The differences can range up to several percent. This result was confirmed by more than a thousand molasses

samples analyzed in the same laboratory. Chromatography beet extract differs, but this product is a highly purified material and has different physical properties than cane molasses. The thin film drying method gives figures very similar to the purge and trap method which is similar to the vacuum oven drying official method. The other analyses showed that there was very little degradation of the molasses compounds during the drying, and thus confirmed that the lower solids values in methods 2 and 3 was not due to a degradation of product.

Table 9. Solids determination with different methods (Vercellotti et al. 1998)

Molasses	Refractometer °Brix	Purge and trap method	Thin film vacuum oven	% difference from °Brix	% difference from purge
Louisiana	80.2	78.49	78.34	-2.05	-0.15
	80.2	78.62	78.47		
Nepal	76.6	72.31	72.21	-5.75	-0.14
	76.6	72.16	72.02		
Mexico	80.2	74.43	74.29	-7.53	-0.14
	80.2	73.88	73.74		
Venezuela A	81.5	75.39	75.25	-7.52	-0.14
	81.5	75.34	75.19		
Venezuela B	80.3	77.15	77.00	-3.96	-0.15
	80.3	77.09	76.94		
Ion beet extract	68.3	68.52	68.39	+0.22	-0.13
	68.3	68.38	68.25		

As a consequence, if refractometric solids (RDS) gives values up to 2% higher than the reference method, the non-sucrose to water (NS/W) ratio calculated for Louisiana molasses is modified (**Table 10**). An over-estimation of 2% on solids involves a NS/W ratio over-estimation of nearly 10% which is significant. With a 7% dry solids over-estimation as for molasses from Mexico and Venezuela (**Table 9**) a 30% NS/W ratio over-estimation would be obtained.

Table 10. Evaluation of the consequence of solids content error on the NS/W ratio. Initial values from Iqbal and Andrews (2000).

Sample	1	2	3	4	5	6	7
Solids (refractometer)	85.3	78.4	83.6	82.8	81.2	81.8	80.4
Water (water%/molasses)	14.7	21.4	16.4	17.2	18.8	18.2	19.6
Sucrose (%solids)	42.4	31.18	38.34	42.80	44.38	40.57	47.81
Sucrose (%molasses)	36.16	24.44	32.05	35.44	36.04	33.18	38.44
Non-sucrose (%molasses)	49.13	53.95	51.54	47.62	45.16	48.61	41.96
NS/W (non-sucrose/water)	3.34	2.50	3.14	2.77	2.40	2.67	2.14
Assuming a 2% over-estimation of solids by refractometry							
Corrected solids : $0.98 \times \text{Brix}$	83.59	76.83	81.93	81.14	79.58	80.16	78.79
Corrected water (%molasses)	16.41	23.17	18.07	18.86	20.42	19.83	21.21
Corrected sucrose (%molasses)	35.44	23.96	31.41	34.73	35.32	35.52	37.67
Corrected non-sucrose (%molasses)	48.15	52.88	50.51	46.44	44.26	47.64	41.12
Corrected (NS/W)	2.93	2.28	2.79	2.46	2.17	2.40	1.94
Δ (NS/W) in % :	14.0	9.7	12.5	12.6	10.6	11.2	10.3
$[(\text{NS/W}) - (\text{NS/W})_{\text{corrected}}] / (\text{NS/W})_{\text{corrected}}$							

A similar phenomenon was observed with French beet molasses (**Table 11**). Mathlouthi and Genotelle (1995) also highlighted the influence of impurities on solids determination. The measured value of solids is as much higher than the true value (obtained by dessication in an

oven or by Karl Fisher titration) as the impurity content increases. These discrepancies are also of major importance when comparing the viscosities of pure and impure solutions.

Table 11. Average French beet molasses solids during the 1991-92 campaign (UCB data)

Factory	1	2	3	4	5	6	7	ave
Sucrose (%melasse)	50.24	49.93	49.77	55.33	49.06	46.64	53.23	50.60
Solids (refractometer)	79.73	80.95	81.80	75.50	79.73	79.93	77.35	79.28
Solids (Karl Fisher)	78.12	78.98	80.13	74.50	78.06	78.26	76.45	77.79
Solids (oven 105°C)	77.59	78.48	79.75	74.03	77.14	77.84	76.31	77.31
Brix after deaeration and dilution 1:5	81.65	82.10	82.65	79.85	81.15	82.05	79.45	81.27

1.2.2 Sugars

Sucrose

It is well known that the Lane and Eynon method for sucrose determination over-estimates true sucrose in molasses (Ravno and Lionnet 1982). This has been attributed in part to the presence of oligosaccharides such as kestoses, which also hydrolyze and react as reducing substances, thereby inflating the sucrose figure. It has also been shown that the kestose concentration in final cane molasses varies from month to month and tends to be higher toward the end of the season.

Reducing sugars

It has also been established that the Lane and Eynon analysis for reducing sugars is consistently higher than can be accounted for by invert alone (Ravno and Lionnet 1982). The magnitude of this difference is not constant and has been shown to be a function of the non-fermentable reducing substances content of molasses, which is typically higher in the early part of the season.

The values given by Rein and Smith (1981) in their study on molasses exhaustion is a good illustration of the differences induced by the measured method itself (**Table 12**).

Table 12. Sucrose and invert concentration differences of boiled down cane molasses samples depending on the method (Rein and Smith 1981)

In %	Average	Min	Max	deviation
Total solids (vacuum oven drying)	86.78	84.48	90.01	0.89
Sucrose (Lane and Eynon)	31.79	27.63	34.96	1.70
Sucrose (gas chromatography)	30.21	26.45	33.83	1.62
Reducing sugars (Lane and Eynon)	19.56	11.98	28.68	3.50
Glucose (gas chromatography)	5.93	2.29	10.86	1.89
Fructose (gas chromatography)	8.69	5.14	13.45	1.70
Sulphated ash	16.75	14.23	19.47	1.12
Viscosity at 40°C (Pa.s)	430	320	520	36

1.3 VISCOSITY-CONSISTENCY OF MOLASSES AND MASSECUITES

1.3.1 Definitions (ICUMSA 1994)

Nomenclature associated with viscosity can be confusing. We first note ICUMSA nomenclature and try subsequently to reconcile the vocabulary used by different authors (**Table 13**).

Table 13. Nomenclature for rheological characterization

Letter	Definition (units)	equation
τ	shear stress (Pa)	
γ	shear rate (s^{-1})	
η	viscosity of Newtonian fluid (Pa.s)	$\tau = \eta \cdot \gamma$
K	consistency (Pa.s ⁿ)	$\tau = K \cdot \gamma^n$
n	flow index	
γ_{corr}	corrected shear rate at the interface (s^{-1})	
η_{app}	Apparent viscosity (s^{-1})	$\tau = \eta_{app} \cdot \gamma_{interface} = \eta_{app} \cdot \gamma_{corr}$

For Newtonian fluids, a constant proportionality exists between the shear stress (τ) and the shear rate (γ) in laminar flow viz :

$$\tau = \eta \cdot \gamma \quad \text{with } \eta \text{ constant viscosity equal to } \eta = \frac{\tau}{\gamma}$$

For non-Newtonian materials, the velocity gradient varies near the interface of the liquid and the shear inducing element (e.g. rotating cylinder). The viscosity is no longer constant but depends upon the shear stress or shear rate (ICUMSA 1994). An absolute measurement of the viscosity of a non-Newtonian material requires that a correction for the change in shear rate be made and the viscosity (or consistency) is determined over a range of shear rates.

$\eta = \frac{\tau}{\gamma}$ is no longer constant, but it is possible to define an apparent viscosity η_{app} for the shear rate

$$\text{at the interface: } \eta_{app} = \frac{\tau}{\gamma_{interface}} \text{ or according to ICUMSA (1994) } \eta_{app} = \frac{\tau}{\gamma_{corr}}$$

with τ : true shear stress at the interface and γ_{corr} corrected shear rate at the interface

When describing the rheological properties of non-Newtonian material, it is therefore necessary to specify the shear conditions under which the viscosity is measured.

Generally non-Newtonian flow behavior is described by the flow curve which is the plot of shear stress (τ in Pa) vs shear rate (γ in s^{-1}) (**Figure 2**) and is mathematically represented by the Power Law model as follows :

$$\tau = K \cdot \gamma^n$$

- K is the Consistency (Pa.sⁿ). The higher the value of K, generally the more viscous the material. Consistency K is an intrinsic characteristic of the fluid independent of the shearing

strain applied during the measuring period. The value of K is obtained by plotting the natural logarithm of shear stress (τ) versus the natural logarithm of shear rate (γ), namely $\ln(\tau)$ versus $\ln(\gamma)$, using linear regression analysis. The exponential of the constant (intercept) obtained from the regression is equal to the consistency (**Figure 3**).

- n : flow index (dimensionless). This is the degree of non-Newtonian behavior. For pseudoplastic fluids, the flow index n lies between zero and unity with values further removed from unity indicating a more pronounced non-Newtonian behavior.

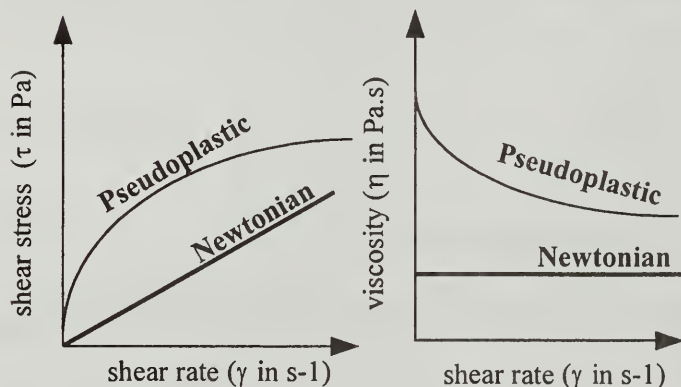


Fig.2 : Viscosity flow behavior of a pseudo plastic fluid (from Pomeranz and Meloan 1982)

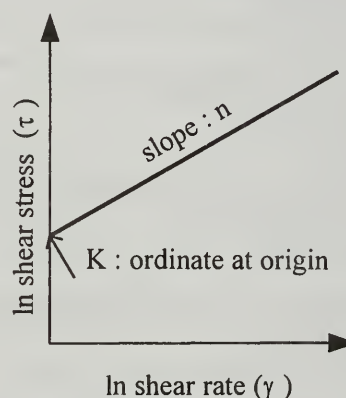


Fig.3 : Evolution of $\ln(\tau)$ vs $\ln(\gamma)$

Molasses often exhibits pseudoplastic or shear thinning flow behavior, i.e. the apparent viscosity of the molasses reduces as higher rates of shear are applied (figure.3). Since the consistency, K , and the index flow, n of a molasses have been determined in a shear rate range, it is possible to determine the apparent viscosity for a shear rate :

$$\eta_{app} = K \cdot \gamma^{n-1}$$

1.3.2 Viscosity measurements

Much experimental work has been performed on molasses to determine viscosity behavior and to propose a mathematical representation. It is important to remember overall that each equation is related to the molasses studied and the analytical methods used in particular for solids and viscosity.

Nowdays most laboratories use a Brookfield viscometer. The Brookfield HBT viscometer measures consistency by measuring the force required to rotate a spindle in the test material.

- the force or drag indicated by a pointer which is attached to the spindle shaft is directly proportional to the shearing stress (τ in Pa).
- the speed of rotation is directly proportional to the shear rate (γ in s^{-1}).

Thus, a speed of rotation versus dial reading plot is comparable to a flow curve (Durgueil 1987). Conversion factors supplied with the instrument enable dial readings to be converted to common viscosity units.

Cautions :

- Necessity to measure at different shear rates. Viscometers are usually calibrated with Newtonian fluids and any fluid will be considered to be Newtonian if measurement is made only at one speed. It is necessary to relate the shear rate and stress to the torque and rotational speed if the fluid is non-Newtonian. As in a sugar factory the shear rates are in the following range (1 s^{-1} for pipeline work flow, 5 s^{-1} during charging of batch centrifugals, 10 to 100 s^{-1} in the molasses film on crystals during centrifuging), it is more convenient to measure in the range $1\text{-}10 \text{ s}^{-1}$ (Broadfoot, *et al.*, 1998).
- Necessity to measure after a delay. Molasses shows thixotropic effects, with the torque reading falling with the increasing time of flow. To avoid variations in the measurement due to thixotropy, it is recommended that the sample be left to reach a steady temperature and to be allowed to rotate for at least 10 minutes after immersion of the spindle before reading the torque.
- Necessity to deaerate. Entrapped air increases molasses viscosity. Deaeration involves boiling the sample under vacuum for a short period, possibly with addition of anti-foaming agents. Sample preparation must be precise and defined.
- Necessity to dissolve crystals of sucrose in molasses. Crystals modify the viscosity and molasses is often warmed to dissolve crystals before the viscosity is measured.
- Necessity to pay attention on the viscometer system. The type of viscometer and even of spindle induces quite high differences in the determination of viscosity characteristics. Barker (1998) studied two viscometers: Brookfield disc spindle (DSV) and Brookfield cone and plate spindle (C&P). The C&P confirmed the Newtonian behavior of pure sugar solutions ($n=1$) whereas the disc spindle one (DSV) read the solutions as non-Newtonian ($n=1.4$). On final molasses the results identified the following: the DSV measured higher consistencies (average 50% higher) than the C&P for all samples; the C&P showed molasses closer to Newtonian ($n=0.9$) when compared with the DSV; the flow behavior index, n , remained constant with the C&P but varied when the DSV was used. The C&P spindle is then recommended.

Nevertheless, for factory control work, rheological measurements using the Brookfield viscometer with disc spindles is often the preferred method, owing to the substantially reduced time required for the measurements. Broadfoot *et al.* (1998) showed, however, that consistency value could be about 30% higher than would be experienced in pipe flow and the flow index value, n , slightly lower.

1.3.3 Molasses viscosity

According to Mathlouthi and Genotelle (1995), pure sucrose solutions have Newtonian behavior and the viscosity is obtained by :

$$\log_{10} \eta = \left(22.46 \cdot M - 0.114 + \phi \cdot \left(1.1 + 43.1 \cdot M^{1.25} \right) \right) 10^{-3} \text{ with}$$

$$\eta \text{ in Pa.s, } \phi = \frac{30 - T}{91 + T}, M = \frac{\text{mol sucrose}}{\text{mol molasses}} = \frac{DS}{1900 - 18 \cdot DS}$$

DS : % dry solids, T : temperature (°C)

Tables and equations on molasses viscosities may be found, but attention must be paid because, as was said before, molasses are non-Newtonian fluids and the shear rate used for the measurement of the apparent viscosity has to be specified.

1.3.3.1 Beet molasses

An important review on viscosity of beet molasses has been written by Mathlouthi and Kasprzyk (1984) and completed by Mathlouthi and Genotelle (1995). McGinnis (1978) in his review on beet molasses exhaustion considered this aspect also. Only some points are reported here.

For impure beet sucrose solution :

$$\log_{10} \eta = \left(22.46 \cdot M^* - 2.114 + \phi \cdot \left(1.1 + 43.1 \cdot A \cdot M^{*1.25} \right) \right) 10^{-3}$$

$$\text{with } \eta \text{ in Pa.s, } \phi = \frac{30 - T}{91 + T}, M^* = \frac{DS^*}{1900 - 18 \cdot DS^*} \text{ with } DS^* = DS \cdot \phi \cdot \left[k + (1 - k) \cdot \frac{P}{100} \right]$$

$$A = 0.85 + 0.15 \cdot \frac{P}{100} \quad \text{with } k : \text{coefficient to adjust the equation, } P : \text{purity}$$

According to McGinnis (1982) viscosity of molasses approximately doubles with each increase of 2 percent in solids. Similarly, lowering the temperature by 10°C doubles the viscosity.

Beet molasses viscosity data are given in **Tables 14** and **15**. Viscosities are generally lower than 10 Pa.s. At the same solids percentage, viscosity of impure beet sugar solutions decreases as the purity decreases. The high viscosity of low purity massecuites is due to their solids content and not to the presence of non-sucrose (McGinnis 1982).

It is also important to study the evolution of the viscosity in saturated solution. As reported by Mathlouthi and Genotelle (1995), viscosity of saturated and supersaturated solutions increases as purity decreases (**Figure 4**). It can be observed that saturated viscosity dependence on temperature does not follow the same behavior for high and low purity products. For purities close to 100%, viscosity decreases as temperature is increased above 80-90°C. However, for lower purities, it may be observed that viscosity reaches a minimum, and this minimum takes

place at lower temperature for lower purities. The optimum is situated at 40°C for purity as beet molasses (around 60). This temperature is the usual end of cooling of the low grade massecuites.

Table 14. Beet molasses viscosities in Pa.s (McGinnis 1982)

Temperature	40 °C		50 °C		60 °C		70 °C	
% solids	70 purity	60 purity	70 purity	60 purity	70 purity	60 purity	70 purity	60 purity
74	0.261	0.250	0.135	0.131	0.079	0.077		
76	0.456	0.435	0.221	0.210	0.125	0.121	0.075	0.074
78	0.863	0.806	0.400	0.376	0.207	0.200	0.119	0.115
80	1.830	1.690	0.777	0.726	0.375	0.359	0.205	0.199
82	4.340	3.960	1.700	1.570	0.756	0.719	0.374	0.361
84	12.400	11.200	4.200	3.880	1.710	1.630	0.785	0.756
86		40.000		12.000		4.310	1.880	1.810

Table 15. Average French beet molasses viscosities during the 1991-92 campaign (UCB data)

Factory	1	2	3	4	5	6	7	ave
Sucrose (%mass)	50.24	49.93	49.77	55.33	49.06	46.64	53.23	50.60
Solids (refractometer)	79.73	80.95	81.80	75.50	79.73	79.93	77.35	79.28
Viscosity (Pa.s)								
20°C	5.900	7.750	19.000	7.200	3.600	7.600	2.850	7.700
40°C	1.050	1.200	2.500	1.080	0.650	1.250	0.550	1.183
60°C	0.380	0.410	0.640	0.270	0.270	0.370	0.240	0.369

McGinnis (1978) reported that the minima of viscosity in the constant saturation curves of many tested molasses is in the area non-sucrose to water (NS/W) ratio between 2.5 and 3.

Influence of the non-sucrose compounds on beet molasses viscosity has been investigated by Khvalkovsky (referenced by Mathlouthi and Kasprzyk 1984) under "normal conditions" defined as molasses at 82 Brix, 40°C and 4.4 Pa.s. The proportion and nature of cations determines the reasons for viscosity increase in impure solutions. Their effects increase as follows: $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$. It is combined with that of anions which show increasing influence: $NO_3^- < Cl^- < Glutamate < lactate$. The global effect is linked to the importance of hydration of sucrose and nonsugars as well as the possible formation of sucrose-cation adducts. The effect of some cations and anions on the viscosity of saturated sucrose solutions at 40°C is illustrated in **Figure 5**. It should be noted that Mg^{2+} associated with Cl^- provokes an increase in the viscosity of saturated sucrose solutions more than 11 fold (Mathlouthi and Genotelle 1995). Similarly Mathlouthi and Kasprzyk (1984) reported an investigation of the effect of impurities on Ukrainian beet-molasses viscosities. The tendency was for the viscosity to increase with the calcium ion content, to decrease with alkaline inorganics and to increase with colloids precipitated in alcoholic solutions.

With the improvement of the centrifuges the limit of mother liquor viscosity is 10 Pa.s for discontinuous centrifuges and 30 Pa.s for the continuous ones and even more according to Cronewitz (1973) reported by van der Poel et al. (1998).

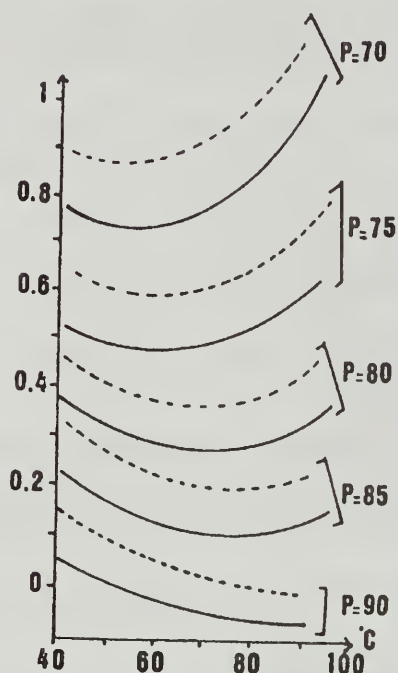


Fig.4 : Variation of viscosity as function of purity and temperature of (——) saturated solutions and (-----) 1.05 supersaturated solutions (from Mathlouthi and Genotelle 1995)

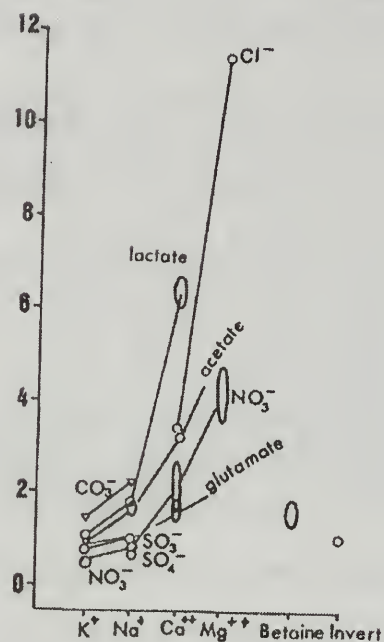


Fig.5 : Effect of some anions and cations as well as betaine and invert on the viscosity of sucrose solutions at 40°C. (hi/hs) is the ratio of impure to pure saturated solution (adapted from Breitung (1956) from Mathlouthi and Genotelle 1995)

1.3.3.2 Cane molasses viscosity

- Bruijn et al. (1980)

They studied the influence of gum on molasses exhaustion. They compared the viscosities of molasses at 50°C and 80% solids with normal concentration of gum (2.5%) in South Africa, particle free and lower gum concentration (by precipitation). The viscosity was 15.9 Pa.s for the original molasses, 8.3 Pa.s for the particle free molasses and 0.48 for the gum free molasses. However, at higher solids concentration the relative contribution of polysaccharides to the molasses viscosity becomes smaller (**Figure 6**). To illustrate this fact, they added 3% soluble potato starch to two samples. At 83.6% solids the viscosity increased from 37 to 57 Pa.s and at 86.6% solids the increase was from 350 to 420 Pa.s. Thus, the influence of the solids content is much more important.

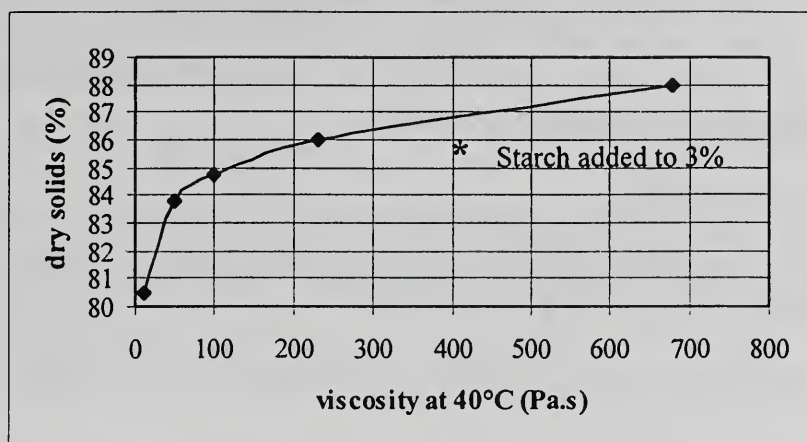


Fig 6: Viscosity of Umfolozi final molasses versus dry solids content (Bruijn et al. 1980)

- Lionnet and Rein (1980) :

Viscosities were measured using a Brookfield HBT viscometer with a No.7 spindle at the same rotational speed of 2.5 rpm and 40°C. It was found that viscosities of Nutsch molasses (pressure filter) could be best correlated in terms of non-sucrose to water (NS/W) ratio :

$$\text{at } 40^{\circ}\text{C} : \eta_{\text{molasses}} = \left(5.94 - 2.86 \cdot \frac{\text{NS}}{\text{W}} + 0.383 \cdot \left(\frac{\text{NS}}{\text{W}} \right)^2 \right) \cdot 10^3 \text{ in Pa.s}$$

- Rouillard and Koenig (1980) :

Viscosities were measured using a Brookfield HBT viscometer with a No.3 spindle and a speed sufficiently high to give an adequate reading. The molasses was degassed. A correlation for molasses viscosities was established. The range of variables considered was as follows (solids 66-89%, true purity 34-68%, temperature 30-73°C, RS/Ash 0.7-1.4, viscosity 0.068-720 Pa.s) :

$$\eta_{\text{molasses}} = \frac{1.03 \cdot 10^{-17} \cdot \left(\frac{\text{DS}}{100 - \text{DS}} \right)^{5.82}}{\left(\frac{T - 273.15}{T^2} \right)^{4.45} \cdot \exp \left(0.187 \cdot \left(\frac{\text{S}}{\text{NS}} \right)^2 + 0.689 \left(\frac{\text{RS}}{\text{Ash}} \right) \right)}$$

DS in%, T in Kelvin

- Broadfoot and Steindl (1980) and Broadfoot, *et al.*, (1998)

They measured viscosities with a Brookfield viscometer with a small adapter in the range (0.2-34 s⁻¹) and three temperatures (40, 50 and 60°C). Molasses used were from different areas of Australia. Their concentration and purity (range 43-81) were modified in a laboratory vacuum pan.

The molasses from the different regions exhibited considerably different viscosities (vary up to 100%) at similar solids, temperature, purity and shear rate. Each molasses showed pseudoplastic flow characteristics with flow index, n , ranging from 0.81-0.88. At lower purity levels the viscosity of each molasses increased.

A multilinear regression was tested :

$$\eta_{app} = k_1 \cdot P^{k_2} \cdot \gamma^{k_3} \cdot \exp\left(\frac{k_4 \cdot DS^*}{k_5 - DS^*}\right) \quad \text{with } DS^* = DS - k_6 \cdot (T - 50)$$

η_{app} : apparent viscosity (Pa.s), DS : %solids, P : true purity, T : °C, γ : shear rate (s^{-1})

The relationship provided a strong correlation with the viscosity data for each mill area and the results of the regression analyses are given for the range values (40-60°C, 43-81 purity) in **Table 16**. But no correlation between the concentration of specific impurities in the molasses and the variation in viscosity was obtained from this study. A multi-variable regression with the data from all the sources was developed nevertheless:

$$\eta_{app} = 0.111 \cdot P^{-1.3} \cdot \gamma^{-0.16} \cdot \exp\left(\frac{3.7 \cdot DS^*}{113.5 - DS^*}\right) \quad \text{with } DS^* = DS - 0.19 \cdot (T - 50)$$

Table 16. Coefficients of the apparent viscosity equation proposed by Broadfoot and Steindl (1980)

Mill	k_1	k_2	k_3	k_4	k_5	k_6	Coeff. Corr
A	28.5000	-2.4	-0.12	3.2	112	0.21	0.998
B	0.0019	-0.4	-0.12	3.9	114	0.19	0.998
C	0.3390	-1.4	-0.15	3.1	110	0.18	0.995
D	1.0780	-1.7	-0.13	3.2	112	0.20	0.997
E	0.3100	-1.5	-0.19	3.9	115	0.18	0.998

This equation was also tested during a study on the rheology of high grade massecuites (Broadfoot, *et al.*, 1998). The first coefficient was found to be 0.088 instead of 0.111 and the flow index n of 0.91 instead of 0.85.

They also observed that entrapped air increases pseudoplastic behavior (n_d) and increases consistency. The mother molasses at the entry of the centrifugal is about twice that predicted for molasses without entrapped air. This confirmed the results of Black and White (1977) who observed that a large amount of bubbles gives a large increase or doubling of viscosity when one volume of bubbles is mixed with two volumes of molasses.

- Barker (1998):

With several samples of molasses from different African mills, Barker (1998) studied the influence of solids content and temperature with two kind of Brookfield viscometers (DSV: disc spindle viscometer and C&P: cone and plate viscometer). The study allowed the proposition of the following equations and conclusions:

- non linear relationship between consistency and solids :

$$K_{DSV} (\text{Pa.s}^n) = 0.740 \cdot 10^{-10} \cdot e^{0.316 \cdot DS}$$

$$K_{C\&P} (\text{Pa.s}^n) = 5.58 \cdot 10^{-10} \cdot e^{0.290 \cdot DS} \quad \text{with DS: \%dry solids}$$

- Temperature is the second most important factor that affects consistency and viscosity of sugar products : consistency of final molasses decreases exponentially as temperature increases and the effect of temperature increases as consistency increases. Using multilinear regression analysis gives the equation :

$$K_{DSV} (\text{Pa.s}^n) = 1.8517 \cdot 10^{-10} \cdot e^{0.3623 \cdot DS - 0.0731 \cdot T}$$

$$K_{C\&P} (\text{Pa.s}^n) = 0.6047 \cdot 10^{-10} \cdot e^{0.3704 \cdot DS - 0.0730 \cdot T}$$

with DS: \%dry solids and T °C between 40 - 66°C

Furthermore, using samples consisting mainly of boiled-down final molasses produced in molasses exhaustion tests, Barker obtained the consistencies (K) and index value (n) reported in **Table 17**. The values of n vary from 0.84 to 0.90 (average 0.88). These values are similar to the ones found by Broadfoot et al. (1998).

Table 17. Typical consistencies of boiled down cane molasses (at 40°C) used in exhaustion experiments (Barker 1998)

Solids (%)	Consistency (Pa.s ⁿ)	n
86.9	168	0.90
86.9	451	0.84
87.2	490	0.84
87.6	265	0.88
87.6	634	0.86
87.7	725	0.85
87.9	399	0.88
89.6	1 272	0.88

Utilization of some relations previously proposed to evaluate molasses viscosity :

With the following parameters (molasses 86%solids and 40 true purity, 40°C temperature, 0.88 flow index n) we calculated (**Table 18**) consistencies and apparent viscosities at four shear rates (1, 5, 10 and 100 s⁻¹) with equations from Broadfoot and Steindl (1980), Broadfoot, *et al.*, (1998) and Barker (1998). Only 1 s⁻¹ was used with the equations proposed by Lionnet and Rein (1980), and Rouillard and Koenig (1980). As we can see, the values fall within a narrow range. It is interesting to observe with Rouillard and Koenig (1980) that viscosity decreases as the RS/Ash ratio increases.

Table 18. Utilization of some relations

	Broadfoot & Steindl (1980)	Broadfoot et al. (1998)	Barker (1998)	Lionnet and Rein (1980)	Rouillard and Koenig (1980)
86% solids, 40 true purity, 40°C			K=222 Pa.s ⁿ , n=0.88		
Apparent viscosity (Pa.s)				only at	1 s ⁻¹
1 s ⁻¹ (pipeline work)	302	239	222	601	324 (RS/Ash=0.5)
5 s ⁻¹ (batch centrifuge)	233	185	183		263 (RS/Ash=0.8)
10 s ⁻¹ (film around crystals)	209	166	169		183 (RS/Ash=1.0)
100 s ⁻¹	144	115	128		163 (RS/Ash=1.5)

⇒ Broadfoot and Steindl (1980) [Australia]:

$$\eta_{app} = 0.111 \cdot P^{-1.3} \cdot \gamma^{-0.16} \cdot \exp\left(\frac{3.7 \cdot DS^*}{113.5 - DS^*}\right) \quad \text{with } DS^* = DS - 0.19 \cdot (T - 50)$$

⇒ Broadfoot et al. (1998) [Australia]

$$\eta_{app} = 0.088 \cdot P^{-1.3} \cdot \gamma^{-0.16} \cdot \exp\left(\frac{3.7 \cdot DS^*}{113.5 - DS^*}\right)$$

⇒ Barker (1998) [Africa]:

$$K_{C\&P} (\text{Pa.s}^n) = 0.6047 \cdot 10^{-10} e^{0.3704 \cdot DS - 0.0730 \cdot T} \quad \text{with } DS (\% \text{ dry solids}), T: 40 - 66^\circ\text{C}$$

⇒ Lionnet and Rein (1980) [Africa]:

$$\eta_{molasses} = \left(5.94 - 2.86 \cdot \frac{NS}{W} + 0.383 \cdot \left(\frac{NS}{W} \right)^2 \right) \cdot 10^3$$

⇒ Rouillard et Koenig (1980) [Africa]:

$$\eta_{molasses} = \frac{1.03 \cdot 10^{-17} \cdot \left(\frac{DS}{100 - DS} \right)^{5.82}}{\left(\frac{T - 273.15}{T^2} \right)^{4.45} \cdot \exp\left(0.187 \cdot \left(\frac{S}{NS} \right)^2 + 0.689 \left(\frac{RS}{Ash} \right) \right)} \quad \text{DS in\%, T in Kelvin}$$

1.3.4 Massecuite viscosity

The important parameter in molasses exhaustion is not the viscosity of the mother liquor only but also of the whole massecuite.

The rheological behavior of the massecuites is different from the concentrated homogeneous solutions. The mathematical treatment of such mixtures is complex and most of the relations given in order to predict the rheological characteristics of massecuite are empirical. They tend to find a correlation between the viscosity (consistency) of the mother liquor (molasses) and that of massecuites:

$$\eta_{\text{relative}} = \frac{\eta_{\text{massecuite}}}{\eta_{\text{molasses}}} \quad \text{or} \quad K_{\text{relative}} = \frac{K_{\text{massecuite}}}{K_{\text{molasses}}}$$

1.3.4.1 beet massecuite

As mentioned by McGinnis (1978), Silina (1953) studied the viscosity of beet low-grade massecuites. She showed that the beet molasses and even the beet massecuite up to 55% crystal content demonstrate a Newtonian behavior. The viscosity of both massecuite and molasses are related by the weight percent crystals (**Table 19**). The more usual percent crystal weight is in the range of 42-46% weight.

Table 19. Influence of crystal ratio on viscosities (McGinnis 1978)

% weight crystals	30	35	40	42	44	46	48
$\eta_{\text{massecuite}}/\eta_{\text{molasses}}$	4.35	6.58	11.24	14.50	19.25	26.30	35.70

Viscosity of beet molasses and massecuites was extensively investigated by Wagnerowski (later McGinnis 1978). He proposed a modified Silina formula :

$$\log_{10} \frac{\eta_{\text{massecuite}}}{\eta_{\text{molasses}}} = 0.01326 \cdot \text{DS}_{\text{massecuite}} \cdot \left(\frac{85}{85 - \text{Cr}} - 1 \right)$$

DS : % solids, Cr : % crystal weight

But Bruhns (1996) reported by van der Poel, *et al.*, (1998) considered that the values of Silina were too high and proposed for the relative viscosity the following equation :

$$\eta_{\text{relative}} = 1 + 2.8 \cdot \left(\frac{V}{V_{\text{max}} - V} \right)^{\frac{4}{3}} \quad \text{with } V : \text{volume fraction of crystals (m}^3/\text{m}^3)$$

and V_{max} : maximal volume fraction (0.62 m³/m³)

1.3.4.2 Cane massecuite

- Awang and White (1976)

They had studied more precisely the effect of the crystal properties: the viscosity of typical massecuites are 3 to 6 times that of the suspending molasses. The major variable is crystal content but also the size of the crystal (mean size and distribution) :

$$\log_{10} \left(\frac{\eta_{\text{massecuite}}}{\eta_{\text{molasses}}} \right) = 1.65 \cdot V \cdot L^{0.15} \cdot \left(1 - \frac{CV}{12} \right) \quad \text{with}$$

$\eta_{\text{massecuite}}$: apparent viscosity of the massecuite

η_{molasses} : apparent viscosity of the mother molasses

V : volumetric ratio of crystal to molasses

L : mean crystal size in mm

CV : coefficient of variation of the size distribution

Lionnet and Rein (1980) :

Viscosities were measured using a Brookfield HBT viscometer with a No.7 spindle at the same rotational speed of 2.5 rpm and 40°C. They found that viscosities of massecuite could be correlated in terms of non-sucrose to water (NS/W) ratio :

$$\text{at } 40^{\circ}\text{C} : \eta_{\text{massecuite}} = \left(10.0 - 2.1 \cdot \frac{\text{NS}}{\text{W}} + 0.08 \text{ crystal content} \right) \cdot 10^3 \text{ in Pa.s}$$

- Rouillard and Koenig (1980) :

They compared different models proposed in the literature and showed that their data on massecuite viscosities (Brookfield HBT viscometer with a No.3 spindle and a speed sufficiently high to give an adequate reading) gave the best fit with the Awang and White model (1976). Nevertheless they suggested the modification of some coefficients to obtain a better fit :

$$\log_{10} \left(\frac{\eta_{\text{massecuite}}}{\eta_{\text{molasses}}} \right) = 2.84 \cdot V \cdot L^{0.0337} \cdot \left(1 - \frac{CV}{12} \right)$$

- Durgueil (1987) :

Consistency and index flow were determined in the range of 40-70°C for C massecuites, C molasses and C Nutsch molasses (pressure filter) (**Table 20**). Massecuites exhibited a smaller degree of plasticity than molasses. In the same way, water seemed to reduce the plasticity by separating the lines of preferential shear and the value of *n* for the Nutsch molasses has been found smaller than for the molasses.

Table 20. Flow index values of cane molasses obtained with a Brookfield HBT viscometer (Durgueil 1987)

Product	n range	n average
C massecuite	0.67/0.81	0.77
C molasses	0.56/0.81	0.73
C nutsch	0.60/0.66	0.63

Molasses showed thixotropic effects, with torque readings falling with the increasing time of flow. They proposed an equation given the massecuite consistency as a function of the pol, the crystal percent and solids.

- Broadfoot and Miller (1990) :

Massecuites were prepared by mixing a known proportion of raw sugar crystals (of mean aperture 0.62 mm and 35% coefficient variation, by sieving) into molasses which had been concentrated in a laboratory pan. For each massecuite the crystal content was 30% weight on massecuite. The rheology of massecuite was studied with a Brookfield viscometer No.7 spindle at 50°C in the shear rate range 0-10 s⁻¹.

Two mother liquors with very high solids content (around 89%) showed very high viscosity (5,700 Pa.s). The values of flow index, n , of the massecuites and of molasses which have comparable dry solids content to the mother liquor were compared and this showed that the flow behavior was largely unchanged.

- Broadfoot et al. (1998) :

During numerous SRI pan stage and centrifuging studies, the rheology of high grade strike massecuites was measured using the Brookfield RVT viscometer with disc spindles.

- Flow index, n , of high grade massecuite (62-75°C and 36-57% crystals) is nearly the same as the mother liquor one.

The relative consistency (K_{relative}) was evaluated as a function of crystal volume fraction. The values were reported (**Figure 7**) as well as previous experimental data on low grade massecuites and the ones predicted with the models of Awang and White (1976) and Metzler (1996). It can be observed that the relative consistencies in high grade massecuite reached values as high as the ones presented previously by Silina in the beet massecuite. In contrast, in the low grade massecuite at fugal entry the relative consistency remained lower than 5 which was in the same range as the data given by Awang and White (1976).

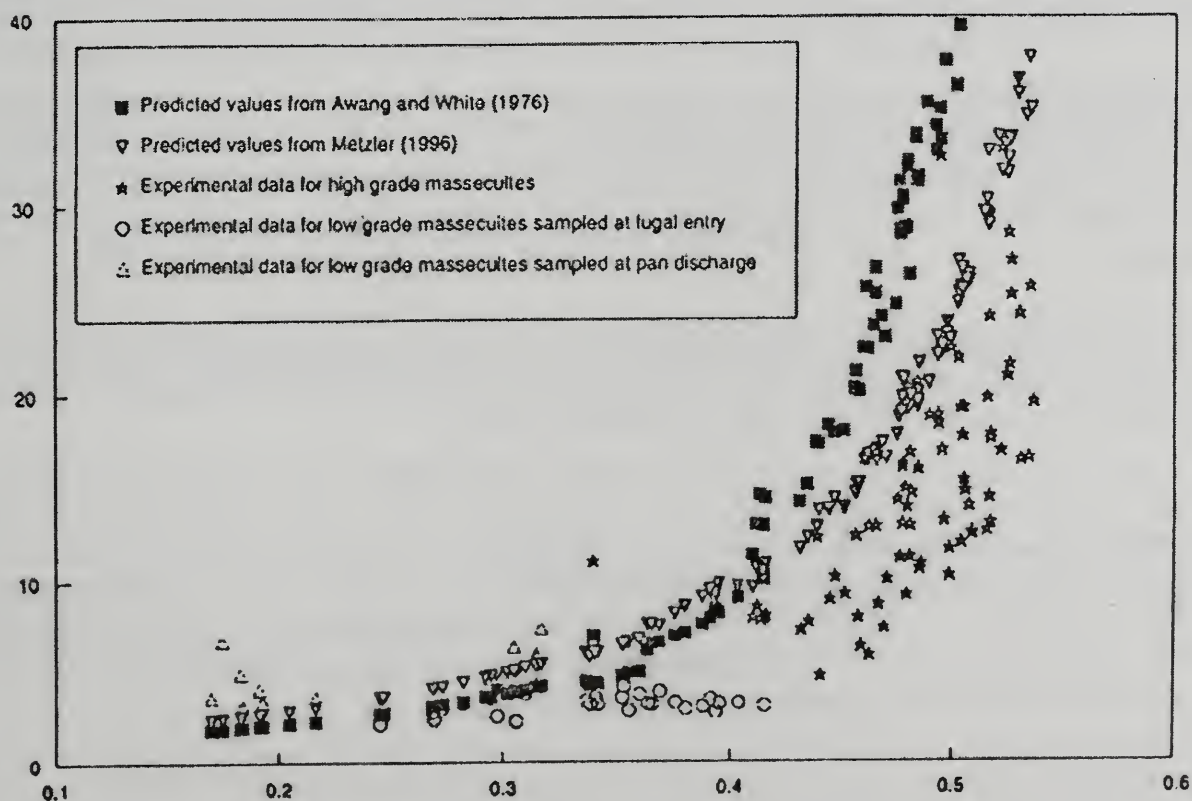


Fig.7 : Relative consistency of different massecuites (Broadfoot et al 1998)

1.3.5 Conclusion on molasses and massecuites viscosities

During the final strike and cooling crystallization, the main factor which limits sucrose crystallization is certainly the viscosity (consistency) of the massecuite. This viscosity (consistency) is mainly linked to the mother liquor (molasses) viscosity and the crystal content.

It is obvious that beet and cane molasses have different rheological behaviors:

- Beet molasses has Newtonian behavior. At the same solids, viscosity of beet impure solution is lower than pure solution but it is inverse if viscosities are compared at saturation or same supersaturation. At low purity and a slight supersaturation (around 1.1) the minimal viscosity corresponds to 40°C temperature. The beet molasses viscosities are around 10 - 30 Pa.s.
- Cane molasses has a slight pseudoplastic behavior with an index flow, n , around 0.88. The apparent viscosity varies with shear rate. This behavior is in part explained by the non-sucrose level and organic macromolecules (dextrans, gums) present.

Several authors measured cane molasses apparent viscosity at 1 s^{-1} shear rates (consistency K) of 300 Pa.s. But according to the pseudoplastic behavior this apparent viscosity decreases to 200 Pa.s at entrance of centrifugals if a 5 s^{-1} shear rate is considered.

The rheological behavior of massecuite is the same as the mother liquor one: Newtonian for beet massecuite and pseudoplastic for cane massecuite. To assess the massecuite viscosity (or consistency for cane massecuite), the ratio massecuite viscosity to mother liquor one (η_{relative} or K_{relative}) is used. The level of this factor is very different for beet and cane low grade massecuites:

- In beet low grade massecuite, as the mother liquor viscosity is low, the relative viscosity that is possible to obtain is high and per consequence the crystal weight content, up to 47% (data reported by Cronewitz (1979) in van der Poel et al. 1998).
- In cane low grade massecuite, since the mother liquor has a high consistency, the relative consistency (K_{relative}) is small and varies in a range from 3 to 6, which means that the crystal level in the final massecuite is more limited. Data of 35% crystal weight content are reported by Van der Poel et al. (1998). To assess the massecuite consistency, Awang and White (1976) proposed an equation which takes into account the crystal volume fraction as well as the crystal size distribution and the coefficient of variation.

Keeping all these points in mind, it is possible to study molasses exhaustion behavior.

2. MOLASSES EXHAUSTION TESTS

Among the research works performed on sucrose solubility in molasses and molasses exhaustibility we focused first our attention on beet molasses, and the test suggested for beet molasses by Wagnerowski often is the so-called "Polish test" which is regularly used in beet sugar factories. In the case of cane molasses, we present the results by country and authors to prevent the interference of the molasses characteristics and methods used. A summary of the most important results are presented at the end.

2.1 BEET MOLASSES EXHAUSTION

Considerable research work into the variables affecting the sucrose solubility coefficient (i.e. composition of the impurity substances, non-sucrose to water ratio and temperature) has been undertaken in the sugar beet industry and has contributed to the technology employed in beet molasses exhaustion. The great bibliographic review written by McGinnis (1978) on that subject will help us to illustrate the differences between beet and cane molasses exhaustion.

2.1.1 Sucrose solubility in beet molasses

According to McGinnis (1978), P.M. Silin, his wife Z.A. Silina and his daughter N.P. Silina developed the melassigenic concept for individual non-sucrose components.

The melassigenic coefficient of a non-sucrose (m_{NS}) is the number of parts of sucrose which is taken in the molasses at saturation per part of non-sucrose for "normal" molasses :

$$m_{NS} = \frac{S}{NS} = \frac{P_m}{100 - P_m} \text{ with } P_m : \text{molasses purity}$$

"Normal molasses" was saturated with sucrose at temperature of centrifuging. The conditions defined by Silin were 40°C and 82% RDS (refractometric dry solids).

The method to determine the melassigenic coefficient of a specific non-sucrose, m_{NS} , was as follow :

- A quantity of the non-sucrose was added to a sample of molasses of initial melassigenic coefficient m_i .
- Solids were adjusted at 82 %RDS.
- Sucrose crystals were then added to make a massecuite.
- Gentle stirring was maintained at 40°C for 3 or 4 days.
- The new molasses was spun off and analyzed the determine the new melassigenic coefficient m_f .
- The melassigenic coefficient of the non-sucrose (m_{NS}) added was then determined.

Example with NaCl :

- Molasses of initial melassigenic coefficient (m_i)

- n kg of NaCl of melassigenic coefficient (m_{NaCl}) are added to the molasses such that n kg are added to $(100-n)$ kg of non-sucrose.
- The melassigenic coefficient after the test is m_f .
- The melassigenic coefficient m_{NaCl} evaluation is based on the sucrose balance :

sucrose linked to the initial molasses	$m_i \cdot (100-n)$
sucrose linked to the added NaCl	$m_{\text{NaCl}} \cdot n$
sucrose linked to the non-sucrose of the final molasses	$m_f \cdot 100$

$$m_i \cdot (100 - n) + m_{\text{NaCl}} \cdot n = 100 \cdot m_f$$

$$m_{\text{NaCl}} = m_i + \frac{100}{n} \cdot (m_f - m_i)$$

n : kg of NaCl added per $(100 - n)$ kg of NS in the initial molasses

Table 21 shows the melassigenic coefficients of various non-sucroses, as determined by Silina.

But in the previous method, when a non-sucrose is added to measure its melassigenic effect, water is also added to maintain the same normal RDS (82% at 40°C) as required in the method. The addition of water solubilizes a fraction of sucrose. The melassigenic coefficient, m_{NS} , takes this phenomenon into account. It is more accurate to deduce the sucrose solubilized by this additive water and to calculate the specific melassigenic coefficient, m_{NS}^* , which is specific for a given non-sucrose composition, and indicates a change in sucrose solubility:

$$m_{\text{NS}}^* = m_{\text{NS}} - 2.35 \cdot (m_{\text{NS}} + 1) \cdot \frac{(100 - \text{RDS}_{\text{normal molasses}})}{\text{RDS}_{\text{normal molasses}}}$$

2.35 is the sucrose solubility at 40°C

$$\text{for a normal molasses 82 brix : } \frac{(100 - \text{RDS}_{\text{normal molasses}})}{\text{RDS}_{\text{normal molasses}}} = 0.2195$$

$$\Rightarrow m_{\text{NS}}^* = m_{\text{NS}} - 2.35 \cdot (m_{\text{NS}} + 1) \cdot 0.2195$$

Table 21. Melassigenic coefficient (McGinnins 1978, McGinnins 1982)

Non Sucrose	m_{NS}	m_{NS}^*	Non Sucrose	m_{NS}	m_{NS}^*
NaOH	4.61	1.69	MgCl ₂	0.65	-2.12
K ₂ CO ₃	3.38	1.10	CaCl ₂	0.56	-0.25
Na ₂ CO ₃	2.88	0.87	Na-products of invert decomposition	0.55	
KCH ₃ COO	2.85	0.84	NaNO ₃	0.42	-0.34
NaCl	2.58	0.72	Invert sugar	0.19	
KCl	2.48	0.67	Ca-glutamate	0.18	-0.48
Betaine	1.03	-0.028	Ca-tyronisate	0.11	
K-lactate	1.02	-0.038	K-tyrosinate	0.09	
K-glutamate	0.99	-0.038	Ca-lactate	-0.14	-0.58
KNO ₃	0.98	-0.056	Ca-acetate	-0.55	-0.78
Na-glutamate	0.93	-0.070	Ca-products of invert decomposition	-0.66	
Na-lactate	0.81	-0.13	Ca(NO ₃) ₂	-1.14	
K-products of invert decomposition	0.70				

As seen in **Table 21**, the coefficient m_{NS}^* is much less important. This indicates that the most melassigenic compound in molasses is the water, and a reduction of the water in the molasses is of prime importance in increasing molasses exhaustion.

One must keep in mind that these values were obtained with a beet molasses and no data were given on the concentration range tested for each non-sucrose. Moreover the modification of the concentration of the other non-sucroses may modify the melassigenic coefficient of the non-sucrose analyzed as noted by Kelly and Keng (1975) in their study on cane molasses (see later).

But if the sucrose solubility decrease induced by a non-sucrose is combined with a reduction of the viscosity, it may be possible to work at higher solids concentration and then to reduce the sucrose lost in the molasses (for example, reducing sugars). Influence on both solubility and viscosity make the interpretation of the phenomenon more difficult.

We can observe that sodium and potassium, which are the most important salts in beet molasses, have the higher melassigenic coefficient. It is why it is common in beet factory to estimate the probable loss of sugar in beet molasses, by the assessment of the several ratios :

- $\frac{\text{Sucrose}}{\text{Na}^+ + \text{K}^+}$ (molar concentration) .
- $\frac{\text{non sucrose} - \text{Ash}}{\text{Ash}} = \frac{\text{organic non - sucrose}}{\text{Ash}}$

As might be expected, high organic factors accompany beet molasses of lower purities.

2.1.2 Importance of the NS/W ratio in molasses exhaustion

As we have seen previously, it is important overall to minimize the quantity of water in the molasses and consequently in the massecuite at the entrance of the cooling crystallizers. In other terms, the non-sucrose to water (NS/W) ratio must be as high as possible. But we have seen in the previous part that the viscosity of the mother liquor increases sharply with the increase of dry solids. We also reported that the minimum viscosity of molasses was around 40°C.

For all these reasons Grut (1953) referenced by McGinnins (1978) suggested a NS/W ratio between 2.8 and 3.2 in the massecuite at the exit of the strike. To reach such a value the mother liquor at pan drop, generally at 75-80°C, must be supersaturated. It is also why in beet sugar, the "optimal molasses reference" used to characterize the quality of the molasses exhaustion is determined at the following conditions: 40°C, NS/W=3 and supersaturation of 1.1.

But to complicate the problem, it has been observed that the solubility coefficient varies with the non-sucrose to water (NS/W) ratio.

2.1.3 Influence of NS/W ratio of the solubility coefficient (SC) in molasses

Solubility of sucrose in each syrup, considered at concentration and temperature within the practical operating range of the factory, has to be determined. But the time required to achieve saturation of syrups of low purity at low temperature, often several months, precludes routine determination of solubility in factory syrups (McGinnis 1982).

Winklund found that the solubility coefficient (SC) in beet molasses remained constant with changes in temperature for syrup of a given non-sucrose to water (NS/W) ratio. This finding, known as Winklund's rule, permits the assessment of the sucrose solubility in impure solutions from determinations made at higher temperature, where attainment of solubility equilibrium is accomplished more quickly, often in a few hours.

According to Wagnerowski. *et al.*, (1962) referenced by McGinnis (1982), it is possible for a molasses issued from a factory to relate the solubility coefficient (SC) with the NS/W ratio as:

$$SC = a \cdot \frac{NS}{W} + b$$

According to Vavrincz (1965) referenced by McGinnis (1978) the linear relationship between solubility coefficient (SC) and non-sucrose to water (NS/W) ratio holds only at ratios above about 1.5. But this fact does not limit the interest of this equation since the NS/W of raw massecuites must, in practice, be held between 1.8 and 3.0.

Others relationships have also been suggested :

$$SC = a \cdot \frac{NS}{W} + b + (1 - b) \exp\left(-c \frac{NS}{W}\right)$$

a, b and c are undimensionless coefficients (table.22)

Table.22 : Solubility coefficient equations

$SC = a \cdot (NS/W) + b + (1-b) \exp(-c \cdot NS/W)$ (reported by McGinnis 1978)

Authors	a	b	c
Schokow	0.234	0.752	2.85
Grut	0.178	0.820	2.10
Nees	0.322	0.563	1.60
D'Orzi	0.271	0.767	1.50
Schwerbljanski	0.287	0.797	2.10
Silin	0.354	0.516	2.00
Wagnerowski et al	0.200	0.750	1.69

Vavrincz (1978) (reported by Bubnik and Kadlec 1995) summarized the results of the investigation of sucrose solubility in impure beet solutions and computed values of coefficients a, b and c for each of the groups examined data. The coefficients varied by a large range :

a from 0.20 to 0.43 average : 0.292
 b from 0.43 to 0.83 average : 0.691
 c from 1.36 to 2.85 average : 1.80

The differences between curves do not allow unambiguous application of the solubility values. In addition, the results of some authors show that the curve is not independent of temperature and consequently the choice of the solubility data is further complicated.

Some authors have shown that the solubility coefficient from beet factories is considerably higher than solubility in the tables of Grut or others for syrups of the same purity. The difference in part must be due to differences in analytical methods (sucrose and solids). Grut determined dry substance by oven drying (McGinnis 1982).

Bubnik and Kadlec (1995) measured the sucrose solubility in beet molasses. The technique used was based on equilibration of the solution in a sealed tube in the presence of crystals of 0.6 mm size in a controlled temperature water bath and with agitation from end to end.

They proposed two different equations according to the non-sucrose to water (NS/W) ratio:

$$\frac{NS}{W} < 0.864: SC = 1 - 0.1387 \cdot \frac{NS}{W} + 0.1606 \cdot \left(\frac{NS}{W}\right)^2$$

$$\frac{NS}{W} > 0.864: SC = 1 + 0.1659 \cdot \left(\frac{NS}{W} - 0.864\right)$$

As shown in **Figure 8** reported by McGinnis (1978) NS/W ratio cannot explain the whole variation of sucrose solubility and the different kinds of impurities certainly interact.

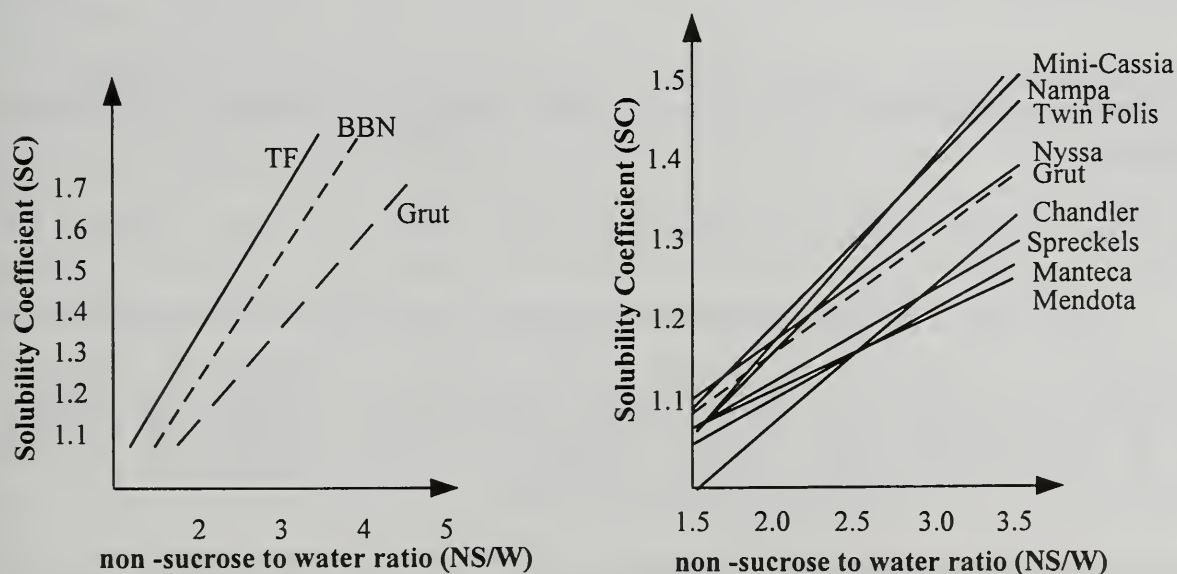


Fig.8 : Solubility coefficients versus non-sucrose to water (NS/W) ratios for different molasses (McGinnis 1978)

2.1.4 Estimation of the molasses exhaustibility with Polish test

To take into account the whole influence of the impurities on molasses exhaustibility, Wagnoroski (1962) proposed a test, so called the "Polish test" which is based on :

- the estimation with the non-sucrose of the molasses of the function between the solubility coefficient (SC) and the non-sucrose to water (NS/W) ratio in the convenient range from 2.2 to 3.2,
- the assessment of the characteristic of the "optimal molasses" at the following conditions : 40°C, NS/W=3 and supersaturation of 1,1.,
- the comparison with the molasses produced in the factory. A molasses is well exhausted if the difference between its purity and the target purity is less than one unit.

Procedure :

- Concentration under vacuum at 80-90°C of about 1.5 kg of molasses to get a NS/W at 3.2 which gives refractometric dry solids (RDS) about 88.2%.
- Separation into 4 crystallizers with about 250g in each.
- Addition to each the required quantity of water according to the NS/W ratio fixed (2.2 – 2.4 – 2.8 – 3.2) and 60 g screened coarse sugar. The apparatus is tightly closed and placed in a thermostatically-controlled bath.
- The temperature is held at 65°C for 15 hours with continuous stirring.
- A sample of crystal-free liquid is drawn through a filter tube and analyzed (sucrose by polarisation, solids by refractometry) to assess the exhaustion quality as explained previously.

In that test it is important to note that the solids are measured by refractometry. Evaluation of NS/W ratios is then different from ones determined with vacuum oven dried solids, as we highlighted earlier.

2.1.5 Conclusion on beet molasses exhaustion

Overall, the most important parameter is the NS/W which must be as high as the consistency of the massecuite permits. According to the increase of the solubility coefficient (SC) with the decrease of the purity, the optimal NS/W ratio is around 3 and the optimal cooling temperature is around 40°C. If a higher temperature is chosen, saturation dry solids increases and the final molasses viscosity may be higher as we have seen in **Figure 4**.

The nature of the non-sucrose may modify the sucrose solubility or the molasses viscosity which explains the differences in exhaustion among the different countries. The "Polish test" allows global consideration of this parameter.

Lastly, one must remember that other parameters influence molasses exhaustion such as the crystal weight content, which must be enough to obtain a good surface area but not too high because of the massecuite viscosity. Values as 40% weight crystal at pan drop are common.

But Wagnerowski (1983), referenced by Mathlouthi and Genotelle (1995) considered that massecuite viscosity is not a fundamental parameter in optimizing beet molasses exhaustion as it is possible to make a preliminary centrifugation of low-grade massecuite.

2.2 CANE MOLASSES EXHAUSTION

Most of the work published on cane molasses exhaustion has been conducted in:

- Australia (SRI) [Broadfoot and Steindl 1980, Broadfoot, *et al.*, 1983, Broadfoot 1984, Broadfoot and Miller 1984, Miller, *et al.*, 1998, Miller, *et al.*, 2000]
- South Africa (SMRI and Huletts company) [Bruijn 1977, Bruijn, *et al.*, 1980, Lionnet and Rein 1980, Wright 1980, Rein and Smith 1981, Ravno and Lionnet 1982, Smith 1995, Sahadeo 1998, Schultz and Eyde 2000)].
- Few from other countries (Saska, *et al.*, 1999).

As the main correlations were obtained with cane molasses from different countries, we chose, as previously, to distinguish the results by countries.

2.2.1 Studies performed in Australia (SRI)

2.2.1.1 Broadfoot and Steindl (1980)

These authors performed a study on solubility-crystallization characteristics of Australian cane molasses. In their opinion, the effect of non-sucrose on the solubility of sucrose in cane molasses has attracted less attention than in the beet sugar industry.

Generally, it has been regarded that within the range of concentration encountered in normal factory crystallization, the solubility reduction at higher non-sucrose concentration levels is due to the predominant influence of the reducing sugars present in cane molasses. It is considered that reducing sugars lower the solubility of sucrose and most inorganic salts increase the solubility. Because of this pattern, the solubility of sucrose in cane molasses is often related to the relative proportion of the reducing sugars to inorganic substances (RS/Ash).

Broadfoot and Steindl (1980) pointed out that some authors (Kelly 1959) agreed that several inorganic salts, particularly those which form stable hydrates (calcium, chloride, magnesium sulphate), decrease the solubility of sucrose. It is therefore necessary to consider the nature of the inorganic salts in the molasses, as well as their total concentration.

They also conducted a study on sucrose solubility in impure cane solutions.

Procedure to assess the solubility coefficient values :

- Composites of final molasses samples were collected from individual mills.
- A subsample of approximately 1 liter from each composite was concentrated under a vacuum of -86 kPa in a rotary film evaporator until the saturation temperature was in the range 47-49°C. To determine the temperature saturation they used the method developed by Wright (1980) based on a photometric way to detect the temperature of re-solution.

- Approximately 700 mL of concentrated molasses was transferred to a container and 150 g of sieved high pol sugar (range 0.4-1 mm) was added.
- The container was sealed and tumbled in a temperature controlled water bath held at 50°C for approximately 20 hours.
- An additional equilibrium trial was conducted for each molasses in a second water bath apparatus held at 65°C. The molasses in that case had previously been concentrated to a saturation temperature of approximately 62-64°C.
- A sample of each equilibrated molasses was obtained subsequently by pressure filtration.

The above procedure was repeated for higher purity molasses obtained by dissolving refined sugar in the original composited final molasses. The supplemented samples were approximately 50, 55, 62, 70 and 80 true purity. The modification of the purity induced a modification of NS/W ratio. In this method, molasses reaches equilibrium from the unsaturated state.

Results on sucrose solubility :

Contrary to Winklund, the solubility coefficient (SC) increased with temperature although this effect depended to some extent on the composition and amount of impurities.

The value of SC was determined at 50°C and 65°C at different non-sucrose to water ratios. No evidence of increased solubility at high NS/W values was observed and an optimization search on the parameters has indicated the expression :

$$SC = 1.0 - \left(\frac{5.75}{T} \right) \cdot \left(\frac{NS}{W} \right)^{\left(0.1 + 0.28 \cdot \frac{RS}{Ash} \right)}$$

$$T = 50 \text{ and } 65^\circ\text{C}; 0.5 < \frac{NS}{W} < 3.5; 0.68 < \frac{RS}{Ash} < 1.71$$

Because SC measurements were conducted at only two levels of temperature, the sensitivity of SC to changes in temperature was assumed and care should be exercised in extrapolating SC values outside the range of conditions.

In this study the authors also examined crystal growth rates and showed that the impurities influence it for the most part because of the change of viscosity induce by the impurity.

Later, Broadfoot (1984) mentioned unpublished data given the following relationship :

$$SC = 0.975 - 0.286 \cdot \left(\frac{RS}{Ash} \right)_{\text{molasses}} + 0.004 \cdot \left(\frac{RS}{Ash} \right) \cdot \left(\frac{NS}{W} \right)_{\text{molasses}}$$

2.2.1.2 Broadfoot (1984)

In this paper correlations for sucrose solubility and viscosities of massecuite and molasses have been applied to predict the limit to sucrose recovery expected for different operating procedures and to investigate ways by which further recovery could be achieved. It also investigated the

manner in which the high viscosities encountered in the cooling crystallizers impose restrictions on the extent of massecuite exhaustion.

Massecuite viscosity changes during exhaustion:

During cooling crystallization the massecuite viscosity increases markedly. Typically the massecuite viscosity is doubled for each 7-8°C reduction in temperature. **Figure 9a** shows massecuite viscosity values for exhaustion of a pan discharge massecuite (65 purity, 92 dry substance) at curing temperatures of 40°C and 45°C. No allowance is made for any increase in viscosity due to the entrainment of air or "gassing" accompanying sucrose destruction.

The net effect on massecuite viscosity of the increasing crystal content and the reducing solids concentration of the mother molasses during the final curing phase is fairly evenly balanced. Thus, when holding a massecuite at a constant temperature in the crystallizers, the massecuite viscosity is maintained at a similar value, or slightly lowered, as crystallization proceeds. During the same time the supersaturation decreases and the growth velocity decreases. Supersaturation is also indicated in **Figure 9a**.

At the lower curing temperature (40°C) a greater supersaturation driving force exists and further exhaustion is possible. However, this can only be achieved at the expense of processing a massecuite with a much higher viscosity (around 3,500 Pa.s at 40°C against 2,000 Pa.s at 45°C). In practice, economic decisions dictate the maximum massecuite viscosity at about 2,000 Pa.s (pipeline viscosity) or 3,000 Pa.s (with Brookfield rotating spindle viscometer).

Main results of the predicted analysis :

- *Effect of the maximum viscosity (between 1,500 and 2,500 Pa.s)*
By increasing the maximum viscosity which can be processed by 500 Pa.s a further reduction in mother molasses purity of 0.6 is indicated (**Figure 9b**). The exhausted molasses purity always decreases with an increase of the RS/A ratio (studied between 0.4 and 1.8)
- *Effect of massecuite purity on exhaustion (at 2,000 Pa.s and 45°C)*
As would be expected, the results show a diminishing reduction in mother molasses purity as massecuite purities are reduced further (**Figure 9c**). The mother molasses viscosity at the end of the crystallization step is about two-fold for a 6 unit reduction in the purity of the massecuite (500 Pa.s at 61 purity and 300 Pa.s at 67 purity).
- *Effect of NS/W ratio*
At the same massecuite viscosity limit of 2,000 Pa.s it is possible to cool to a lower curing temperature a massecuite of a lower NS/W but the exhaustion is also lower (**Figure 9d**). Thus, it is better to work at high NS/W and high temperature (50°C). It is necessary to boil massecuite at high NS/W ratio, particularly when RS/A ratios are low.

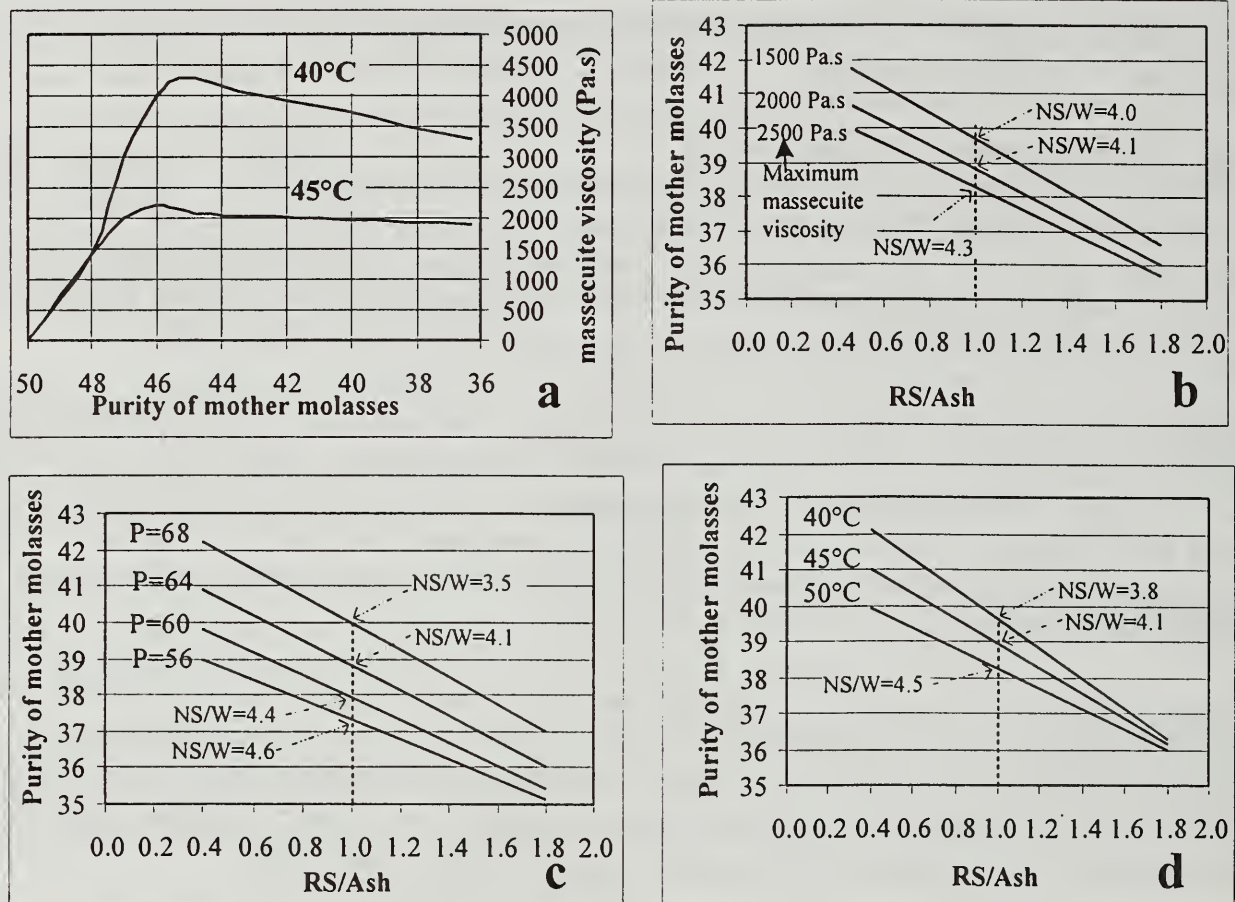


Fig.9 : Viscosity limitations on massecuite exhaustion (Broadfoot 1984)

- (a) variation of massecuite viscosity during exhaustion,
- (b) effect of the limiting massecuite viscosity on exhaustion,
- (c) effect of massecuite purity on exhaustion at the viscosity constraint,
- (d) effect of non-sucrose to water ratio on exhaustion at the viscosity constraint .

2.2.1.3 Broadfoot and Miller (1984)

These authors constructed a new small apparatus to conduct the molasses exhaustion trials.

The crystallizer reservoir (**Figure 10**) is aligned vertically with a top mounted helical stirrer which is normally fully submerged in the massecuite to minimize air entrainment. Each crystallizer holds approximately 3.5 liters of massecuite. The reservoir is surrounded by a jacket through which heating/cooling water is pumped. The heat transfer area/volume ratio is $20 \text{ m}^2/\text{m}^3$ compared with about $2.5 \text{ m}^2/\text{m}^3$ in factory coil crystallizers.

The stirrer is normally driven at a speed of 1.8 rpm. The bottom of the stirrer shaft is located in a recess in the top of a removable cone which is screwed into the base of the crystallizer. This cone occupies a region which would otherwise be poorly mixed by the blades of the stirrer.

Intermediate massecuite samples can be obtained by removing a plug in the base of the crystallizer. At the end of the exhaustion test the top is removed and a water jacketed tube for

pipeline viscosity measurement is inserted in place. No mention is made about the separation of the crystals from the mother liquor. It may be obtained by emptying the vessel from the bottom directly in a pressure filter

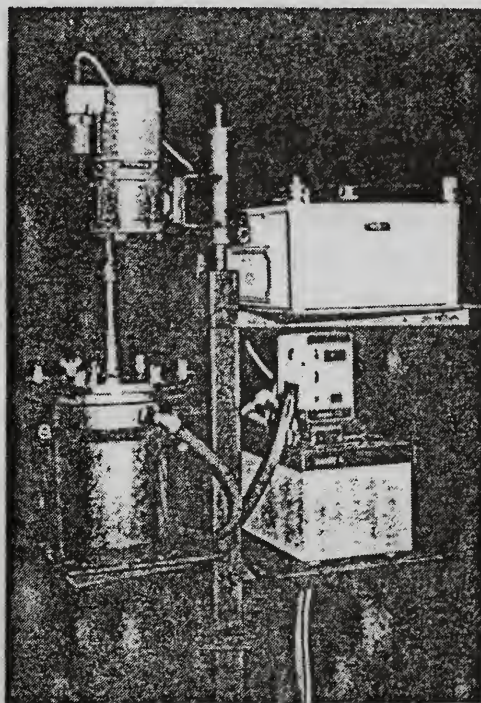
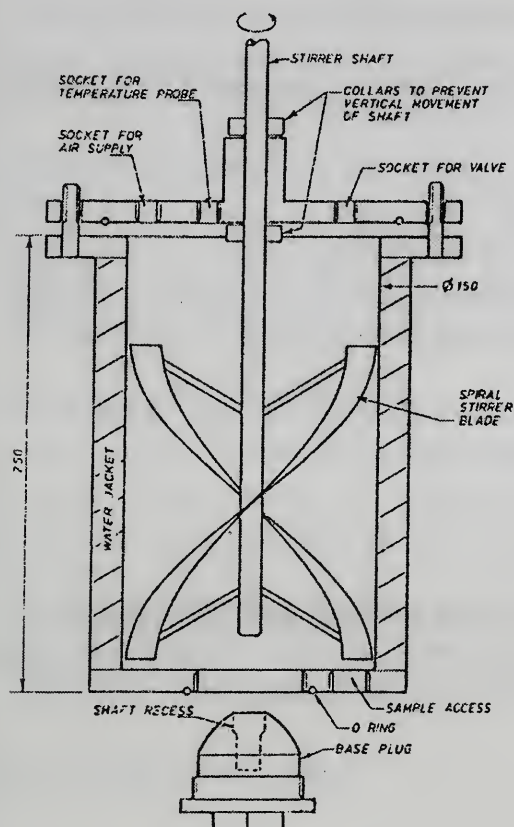


Fig.10 : Exhaustion trials new pilot crystallizer (Broadfoot and Miller 1984) Australia

The performance of factory crystallizers were evaluated by comparison of the exhaustion achieved in the pilot. The standard cooling conditions of massecuites at pan discharge are the following :

- stir at 1.8 rpm
- hold at pan drop temperature for 1.5 hours
- cool at near 2°C per hour, over 16 hours, to 40°C
- hold for 4 hours
- reheat to 55°C and hold for 3 hours.

2.2.1.4 Miller, et al. (1998)

Thes authors studied the exhaustion characteristics of Australian molasses with the apparatus constructed by Broadfoot and Miller (1984).

Method :

- Bulk samples of final molasses, each 40 L, were obtained from 6 sugar producing regions in Australia during the early, middle and later parts of the 1996 crushing season. The material was frozen and stored.
- For each exhaustion trial, pre-warmed molasses was drawn into the pan and boiled in the 15 L vacuum pan to remove entrained air or gas.
- The molasses was evaporated at 70°C to give, in turn, three levels of non-sucrose to water (NS/W) ratios (3.4 - 3.8 - 4.3).
- After the calculated amount of water had been evaporated from the molasses, the contents were heated to 75°C and an aliquot (crystallizer volume of 3.5 L) was removed from the pan and transferred to the pilot crystallizer unit.
- The molasses was seeded with sieved refined sugar, pre-heated to 75°C, to give a crystal content of 20% on massecuite. (*According to the temperature and solids level of molasses, one can assume that some sugar was then dissolved*).
- The crystallizer was then sealed to prevent evaporation. For high NS/W ratios, the molasses was heated to 80°C before seeding to prevent shock nucleation from occurring.
- In all trials, the stirrer speed was 1.8 rpm.
- Material was cooled to 60°C at 2°C per hour, then to 50°C at 1°C per hour.
- Held at 50°C for a total curing time of 24 hours.
- The exhausted massecuites was then pressure filtered to give mother molasses samples for viscosity measurement and analysis.

One can observe that the final temperature is higher than the 40°C suggested previously (Broafoot and Miller 1984)

Analytical methods :

- Dry substance by vacuum oven drying at 60°C for 16 hours.
- Sucrose by double polarisation.
- Reducing sugars by Lane and Eynon method.
- Glucose and fructose by HPIC.
- Viscosity with a Brookfield Synchro-lectric model RTD fitted with a small adaptater and SC4 29/13 spindle, following the procedure outlined in SPS-5 (ICUMSA 1994). The viscosity was measured at several speed settings so that the effect of shear rate on the viscosity could be quantified. Viscosity figures are quoted as Consistency (K).

Proposition of a molasses purity target equation :

In the 54 trials RS/A ratios varied from 0.7 to 2.2 and NS/W had three values (3.4 - 3.8 - 4.3). The target purities were compared at two mother liquor consistencies (100 Pa.sⁿ and 250 Pa.sⁿ). According to the analytical method used for the reducing sugar analysis (Lane and Eynon or gas chromatography), the following equations were obtained :

With NS/W at a consistency of 100 Pa.sⁿ

$$P_{LE} = 41.1 - 8.7 \cdot \log_{10}[\text{RS}/\text{Ash}]$$

$$P_{CG} = 46.9 - 0.5 \cdot [1 - \exp(-1.3 \cdot (F+G)/\text{Ash})]$$

(LE: Lane and Eynon, GC: gas chromatography)

With NS/W at a consistency of 250 Pa.sⁿ

$$P_{LE} = 39.4 - 10.6 \cdot \log_{10}[RS/Ash]$$

$$P_{CG} = 55.1 - 18.7 \cdot [1 - \exp(-2.6 \cdot (F+G)/Ash)]$$

All samples showed a similar trend with the purity of the exhausted molasses decreasing almost linearly with increasing NS/W ratios, over the range of interest (3.2 – 4.3). An extra exhaustion time (from 24 to 48 hours) allowed an extra purity gain of 0.7 at 3.4 NS/W ratio.

Nevertheless, the limit of the NS/W ratio was the maximum consistency of the C massecuite that can be handled by the process equipment. As we have seen previously, the massecuite consistency at a given temperature is a function of the molasses phase and of the percentage of crystal in the material. Crystal size, size distribution and the amount of entrained air will also contribute to the overall massecuite consistency.

Even with the same NS/W ratio and the same standard exhaustion procedure (cooling profile and crystal content) the authors observed that exhausted molasses may have purity differences up to 3.2 units. It may be due to a different composition of impurities. The exhaustibility varies with the season, and increases during the season.

A consistency of 100 Pa.sⁿ at 50°C has been tentatively selected as a level for the mother molasses that most factories could process.

2.2.1.5 Miller, *et al.* (2000)

These authors studied the exhaustion characteristics of Australian molasses with the crystallizers constructed by Broadfoot and Miller (1984) but one was modified to test the influence of shear rate.

Massecuite was sampled in three factories near the product transfer pump. Each pilot unit simulation included a "control" run which followed the procedure outlined by Miller, *et al.*, (1998), viz. cool from pan temperature to 60°C at 2°C/h, then to 50°C at 1°C/h, and hold at 50°C for a total curing time of 24 h.

To test the effect of shear rates one crystallizer was differently controlled: 0.8 rpm up to 60°C then 0.25 rpm. In these conditions shear rate did not have a significant effect on the degree of massecuite exhaustion. For a shorter curing time or for a lower final temperature, the influence of higher shear rates was expected to be more marked, but was not tested.

The influence of the curing time was tested removing a small quantity of massecuite after 6 hours.

- For the 3 cases, there was a rapid purity decline in the first 6 h (about 6 points from 47 to 41).
- The rate of fall then slowed, but substantial further gains were still obtained (down to purity around 37-36), particularly at high NS/W ratio (range of the massecuites tested was 3.3-4.0).

The laboratory and factory trials have confirmed the importance of high NS/W values. For a given final cooling temperature, and total curing time, the mother molasses purity that was achieved was strongly dependent on the NS/W value at the end of the exhaustion test. But it was not obviously the molasses with the higher RS/A ratio which gave the lowest exhausted molasses purity (Figure 11).

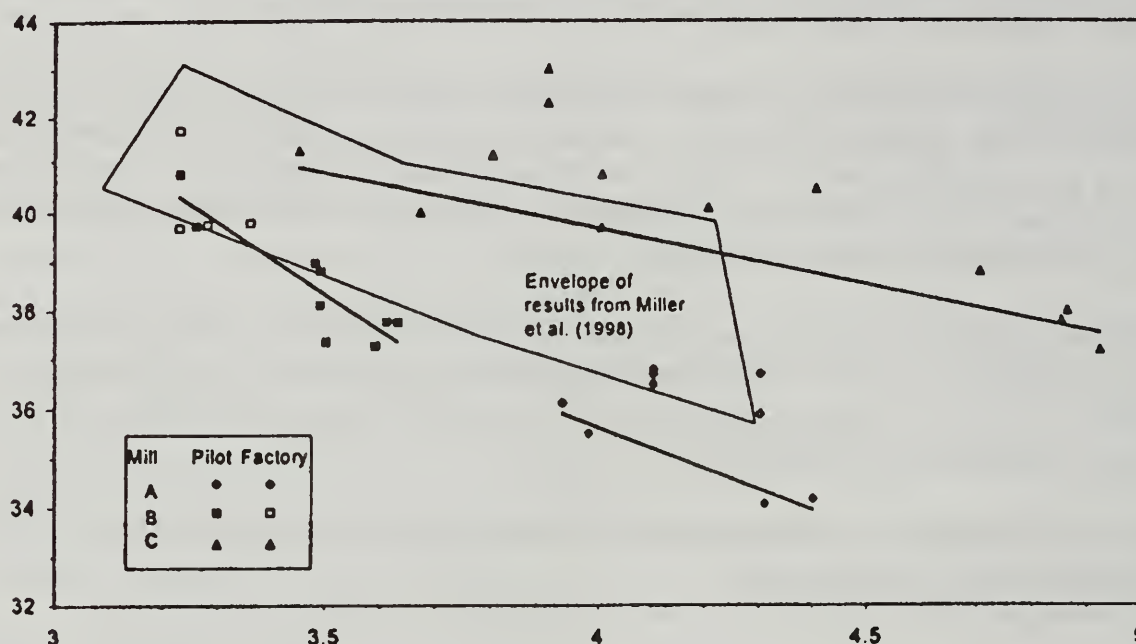


Fig.11 : Exhausted molasses purity levels for various non-sucrose to water (NS/W) ratios from pilot scale and factory crystallizer trials (Miller et al. 2000)

The effect of molasses or water addition combined with lower temperature was also tested. In the pilot scale trials, all at 1.8 rpm, massecuite was cooled from pan drop temperature to 60°C or some other temperature and a pre-calculated amount of molasses or water was then added, in small increments over about 30 min, with the cooling being continued to a lower final temperature than the control run. Typically the amount of diluent added decreased the NS/W ratio by about 0.3 unit. The dilution step accompanied by further cooling did not result in any improvement in the exhaustion achieved. The viscosities of both massecuite and mother molasses at the two test conditions were virtually the same. The molasses consistency range obtained was very large, depending on the factory (55 to 310 Pa.sⁿ).

Preliminary factory trials with careful addition of water to massecuite to assist in flow transfer, rather than employing recycle molasses, showed that similar exhaustion results could be obtained, for the same viscosity reduction and NS/W change. Further factory experimentations into this option should be performed.

2.2.1.6 Conclusion on the exhaustion work performed in Australia

Most of the trials have been performed with the pilot scale crystallizer described by Broafoot and Miller (1984) with a volume of 3.5 liters of massecuite. The last studies have highlighted the

advantage of NS/W for achieving low final molasses purities, particularly if residence time available for exhaustion is limited. Nevertheless this parameter is not the only one, and the relation between exhausted molasses purity and NS/W is quite strong (**Figure 11**) and cannot be explained by the RS/Ash ratio.

The subject is not closed, since recently SRI began an investigation of sucrose solubility and molasses exhaustion using nuclear magnetic resonance spectroscopy (Schultz and Eyde 2000). This probe allows continuous measurement of crystal content in the vacuum pan and knowledge of the balance in the vessel. The objective is to study the phenomenon of sucrose solubility under normal sugar boiling conditions.

2.2.2 Studies performed in South Africa (SMRI and Hulett's company)

2.2.2.1 Lionnet (1978)

The plant (working capacity of 80 L, exchanger surface area of $15\text{m}^2/\text{m}^3$, stirring rotation of 0.25 rpm) was situated directly above a crystallizer at a mill. About 100 liters massecuite was treated in the pilot mixer, over a period of 2 seasons. Cooling of the massecuite was from 65°C to $34\text{--}40^\circ\text{C}$ in 15 hours, solids by vacuum oven and true purity of massecuite and Nutsch molasses were determined.

They showed that massecuite total solids was statistically the most important factor. The second and only other statistically important factor was the residence time : the longer the exhaustion, the better the exhaustion. They obtained the following equation :

$$P_{\text{nutsch molasses}} = a + b \cdot \exp(-c \cdot t) \quad \text{with } t \text{ in hours}$$

$$\text{for B massecuite: } P_{\text{nutsch molasses}} = 38.3 + 9.2 \cdot \exp(-0.20 \cdot t)$$

$$\text{for C massecuite: } P_{\text{nutsch molasses}} = 36.7 + 7.4 \cdot \exp(-0.18 \cdot t)$$

Nevertheless it is noted that the residence time was in all the cases, less than 15 hours, which is quite short.

2.2.2.2 Lionnet and Rein (1980)

The apparatus and the procedure are exactly the same as previously described (cooling from 65°C to 37°C within 15 hours).

The authors studied a massecuite NS/W ratio range from 3.21 to 7.28 (no indication as other authors of molasses NS/W ratios but if the purity of the crystal is taken as 100 it is the same). It is very important to observe that the level of NS/W ratios observed here are very high and the total dry solids of the massecuite may vary from 91 to 96.

Molasses purity was not found to be significantly correlated to Nutsch viscosities. Overall, NS/W was still more highly correlated with molasses purity. Regression analysis yielded the following equation:

$$P_{\text{molasses}} = 44.17 + 1.21 \cdot \left(\frac{\text{NS}}{\text{W}} \right)_{\text{massecuite}}$$

They also correlated the viscosity with the NS/W ratio (see part.1). Viscosities were measured with a Brookfield viscometer at one rotational speed of 2.5 rpm. The Nutsch molasses viscosities were in the range 1,000-3,000 Pa.s which is very high. But these values are at 40°C and the limit given previously was 250 Pa.sⁿ at 50°C. This difference cannot be explain by the temperature difference as the data given in part 1 on molasses viscosity indicated that molasses viscosity doubles with a decrease of 10°C but are not mulitplied by 10.

On the base of theoretical equations, Lionnet and Rein (1980) established a model and assessed some parameters :

- Solubility coefficient (SC)

They obtained for the massecuite a very strong dependence of solubility coefficient (SC) on NS/W, dry solids, purity and RS/Ash. However, only NS/W and RS/Ash were significant :

$$\text{SC} = 0.742 + 0.182 \cdot \left(\frac{\text{NS}}{\text{W}} \right)_{\text{massecuite}} - 0.346 \cdot \left(\frac{\text{RS}}{\text{Ash}} \right)_{\text{massecuite}}$$

Values of SC averaged 1.23 and covered the range 0.86 to 1.62. This conflicts with the general meaning that SC valus in cane molasses are lower than 1. But the authors emphasized that the information reporting that SC is lower than 1 relates to lower NS/W ratios than were found in South African massecuites. Solubility coefficients greater than one were obtained for NS/W higher than 4.5.

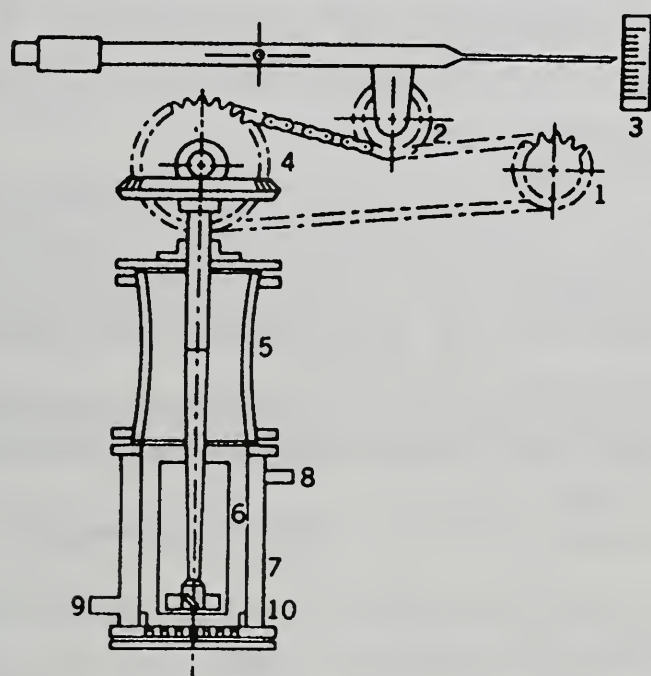
2.2.2.3 Bruijn (1977) and Rein and Smith (1981)

Since that period, most experiments have been performed in South Africa with the apparatus constructed by Bruijn (1977) and the procedure described by Rein and Smith (1981). This apparatus is referenced in the Cane Sugar Hanbook (Chen and Chou 1993).

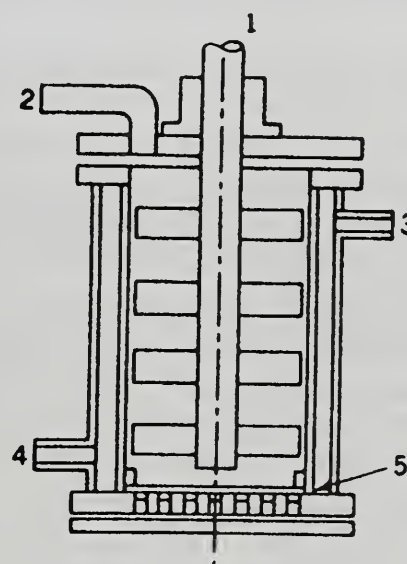
Description of the apparatus (Bruijn 1977)

- The basic component is a 630 mL jacketed vessel which acts in turn as an evaporator, crystallizer and Nutsch bomb (**Figure 12**).
- The vacuum pan was constructed in two parts bolted together. The bottom part is a jacketed cylinder of 630 mL and it is heated by passing steam through the jacket. The top is a quickfit pipe segment of 80*125 mm. To increase the circulation and to measure the mobility of the massecuite, the pan is fitted with a stirrer with a diameter of 40 mm, a speed of 140 rpm and is placed in a tube to increase efficiency. The top cover is further provided with an inlet tube for molasses and one for the addition of sugar crystals. Massecuite temperature is measured by a thermocouple.

- After a massecuite of the required mobility has been prepared, the bottom part of the pan is disconnected and fitted to a stirrer assembly, which avoids the transfer from one vessel to another.
- As the equilibration of the massecuite in the crystallizer requires a much longer time than the concentration in the vacuum pan, there are 4 stirrers run at 12 rpm driven by a common motor.
- During the equilibration period of the massecuite, water of the required temperature is circulated through the jacket of the vessel. The top cover is provided with an inlet for compressed air.



1:driving sprockets 2:idler for torque measurement
3:pointer and scale for torque measurement 4:sprocket and bevel gears driving the stirrer 5:glass pipe section 6:tube for stirrer 7:jacketed lower part of vacuum pan 8:steam inlet 9:steam outlet 10:screen



1:stirrer 2:air inlet 3:water outlet
4:water inlet 5:screen

Fig.12 : Equipement to determine target purity in South Africa (Bruijn 1977)

- After the mixture has reached equilibrium in 48 hours the bottom plate is removed and the mother liquor is separated from the crystals through the bottom screen by compressed air.
- The mother liquor is subsequently analyzed for sucrose and dry matter

Choice of the viscosity of the molasses (Rein and Smith 1981)

As the viscosities were in that case measured with a Brookfield RVF viscometer No.6 spindle at only one rotational speed of 2 rpm, we kept the term viscosity, but it should have been consistency if measurements were carried out at several shear rates (see part 1).

The target viscosity level, i.e. the viscosity level to which the molasses can be concentrated, can have a significant effect on the mother liquid purity. African researchers have recommended a procedure of three boilings on each sample, respectively above, below and as close as possible to 200 Pa.s at 40°C. Exhausted purity would then be determined by the interpolation of a plot of purities against viscosity. While this procedure overcomes the problem of deviation of actual from target viscosity for a single boiling, it also generates a much higher analytical load. The results indicated that the purity was independent of viscosity above 300 Pa.s. A target range of 350-400 Pa.s was thus selected and used for the boiling down tests on molasses. All the experiments were conducted above 400 Pa.s

Description of the procedure followed during the exhaustion tests

- 1,000 mL of molasses was mixed with 800 mL of water.
- 300 mL of the diluted molasses was transferred to the vessel, vacuum applied (-97 kPa) and evaporation started by feeding steam to the jacket. A further 1,200 mL was fed in during the evaporation stage, with the remaining 300 mL in reserve.
- A chain tension measurement was used to indicate when the target viscosity level has been reached (NS/W range from 0.6 to 1.8. only one trial with NS/W of 2.2).
- Evaporation was then stopped and 300 mL of the concentrated molasses was removed for viscosity measurement. 250 mL of bakers' sugar was added to the remainder (about 300 mL) and the vessel transferred to the crystallization stage.
- Water at 40°C was then circulated through the jacket for 48 hours while the massecuite was stirred continuously (at 12 rpm).
- The bottom cover was then removed, exposing the perforated plate covered by a screen, and the vessel pressurized with air to extract a sample of the exhausted molasses.
- Sucrose and reducing sugars by both Lane and Eynon (LE) and gas chromatography (GC) methods. Solids by vacuum oven drying and sulphated ash. Mother liquor viscosity was measured out at 40°C, using a Brookfield RVF viscometer with n°6 spindle at 2 rpm.

Results on the purity target :

The RS/Ash ratio was in the range 0.6 to 1.8. The NS/W was such that the viscosity was higher than 400 Pa.s.

The purity target was slightly different according to the season :

$$1978 \quad P_{GC} = 40.5 - 6.5 \cdot \log_{10}[(F+G)/\text{Ash}]$$

$$1979 \quad P_{GC} = 40.1 - 5.6 \cdot \log_{10}[(F+G)/\text{Ash}]$$

$$1980 \quad P_{GC} = 40.5 - 6.4 \cdot \log_{10}[(F+G)/\text{Ash}]$$

The purity target was significantly different based on the analytical method used to determine purity :

$$P_{LE} = 37.7 - 17.6 \cdot \log_{10}[\text{RS}/\text{Ash}]$$

(sucrose by Lane and Eynon)

$$P_{GC} = 33.9 - 13.4 \cdot \log_{10}[(F+G)/\text{Ash}]$$

(sucrose by gas chromatography)

Introduction of a NS/W ratio term into regressions significantly increased the correlation coefficient above the levels found using RS/Ash ratios alone :

$$P_{GC} = 48.2 - 4.8 \cdot (F+G)/Ash - 2.2 \text{ NS/W}$$

The significant positive correlations indicate that part of the benefit of high reducing sugar levels is that a higher NS/W ratio can be achieved at the same viscosity. Non sugars contribute to viscosity to a much greater extent than do sugars. When reducing sugar levels are high, the proportion of non-sucrose relative to total solids in molasses is low. This must contribute to the relationship between viscosity and reducing sugar content, but it cannot be determined from this work whether it is the sole factor.

The correlation between non-sucrose/water and (fructose+glucose)/ash ratios means that regressions containing both variables, such as that given earlier contain an element of inherent correlation.

2.2.2.5 Smith (1995)

Smith conducted a theoretical study with the purities of molasses obtained during the middle of the 1994 season in South Africa. These molasses had very low RS/A ratios ranging from 0 to 0.6.

He pointed out that the logarithmic target purity formula was fundamentally inappropriate for low RS/Ash ratios and the exponential form was recommended :

$$P_{GC} = 43.1 - 17.5 \cdot \left(1 - e^{-0.74 \cdot \frac{F+G}{Ash}} \right)$$

2.2.2.6 Sahadeo (1998)

Sahadeo used the same apparatus as Bruijn 1977. The aim of this study was to test the influence of the crystallization time and of some non-sucrose components (cations, reducing sugars, dextrans).

He started with a batch of molasses having the following composition: 78.4% solids; 31.9% sucrose, 5.7% glucose, 7.6% fructose, 18.5% organic non-sugars, 2.07% gums, 0.009% starch, 12.7% ash with the following repartition in % solids: 0.09% Na⁺, 2.96% K⁺, 0.33% Mg⁺⁺, 0.83% Ca⁺⁺. Thus, a 40.7 purity and 1.05 RS/Ash ratio.

The composition of the molasses was then modified adding different non-sucrose and an appropriate amount of sucrose to maintain the purity at the same level.

Procedure for the crystallization step :

- Samples were concentrated to 87% dry solids in order to reduce the viscosity effect. With a purity of 40.7 the NS/W ratio was 3.96.

- Castor sugar was added.
- Crystallization for 48 hours minimum at 40°C before separation of the molasses by pressure
- Analysis of solids by vacuum oven drying, sucrose, glucose and fructose by gas chromatography, sulphated ash, and viscosity with a Brookfield cone and plate viscometer at 50°C after dilution to 62% solids.

Target purity formula :

The experimental results obtained with molasses from different parts of Africa showed good agreement with the target purity formula proposed by Smith (1995).

Crystallization time :

The results indicated that 3 days (72 hours) is the optimum time for complete exhaustion to occur.

Addition of Ash :

Different amounts of Na^+ , K^+ , Mg^{++} , and Ca^{++} were added (between 20 to 80mg/kg solids), which induced a reduction of RS/Ash ratio from 1.05 to 0.5.

- The exhausted molasses purities with salt addition were always higher than the ones without.
- The melassigenic effect was in a different order ($\text{Na}^+ > \text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+$) than reported in many previous works, in particular concerning the potassium ion. A possible explanation given by the authors was that Na^+ increases viscosity of solutions whereas K^+ diminishes it, which is in agreement with Chen and Chou (1993).

Addition of Reducing sugars :

Sahadeo tested increasing the RS/Ash by addition of invert, addition of glucose, and addition of fructose.

- The increasing concentration of (G+F)/Ash from 1.1 to 1.3 then 1.5 and 1.8 induced a reduction of molasses purity from 34.6 to 33.9 then to 33.3.
- Nevertheless, the addition of glucose and fructose separately did not give the same improvement, but the author could not explain this phenomena.

2.2.2.7 Conclusion on the exhaustion work performed in Africa

It can be first observed that the molasses purities in South Africa varied from 33 to 39, which is a much lower range than the ones found in Louisiana (around 40-42) (Iqbal and Andrews 2000).

The first experiments conducted on molasses exhaustion were performed during a very short time (15 hours) whereas since 1981 equilibrium purity was researched using crystallization times of 48 hours and even more.

Rein and Smith (1981) outlined the necessity to perform the experiments at high NS/W so that the purity equilibrium is independent of viscosity. It was recommended to work at molasses viscosity higher than 400 Pa.s, but the factory limit is more in the range (55-310 Pa.sⁿ) according Miller, *et al.* (1998 and 2000). In his study, Sahadeo chose to work at 87% dry solids but the

viscosity is not specified. Using the relation proposed by Rouillard and Koenig (1980) it would give around 270 Pa.s (87%DS, 40°C, RS/Ash=1).

Molasses exhaustion is improved when the RS/Ash ratio increases. Rein and Smith (1981) indicated that part of the benefit of high reducing sugar levels was that a higher NS/W ratio can be achieved at the same viscosity. Sahadeo (1998) observed that molasses purity decreased from 34.6 to 33.9 for RS/Ash from 1.05 to 1.5.

2.2.3 Other Countries

2.2.3.1 Japan

Kelly and Keng (1975) considered that in a system with more than one solute we must recognize a system in which the solute entities compete for solvation sheaths. In such competition, substances such as glucose or fructose are more lyophilic than sucrose and have the effect of reducing the solubility of sucrose. With one solute in addition to sucrose, the lower the solubility of the second solute in water the greater the proportion of sucrose in solution. The inorganic solutes are of relatively low solubility thus they increase sucrose solubility. The group of substances covered by the term other organic matter (OOM) has received much less study than the reducing sugars or ash groups chiefly because of the apparent importance of the latter based on simple statistical studies.

Kelly and Keng considered three groups of impurities: reducing sugars (RS), ash (Ash), other organic matter (OOM).

Melassigenic effect appears as an additive function of the melassigenic behavior of all the three constituent groups of impurities. As the three groups are in the molasses we can expect the composition of each group to change with the change in growing conditions of the sugar cane and/or chemical techniques employed in processing.

They suggested that the expected true purity of the molasses as :

$$P = a_{RS} \cdot \left(\frac{RS}{NS} \right) + a_{ash} \cdot \left(\frac{Ash}{NS} \right) + a_{OOM} \cdot \left(\frac{OOM}{NS} \right)$$

The values of the coefficients vary with the country or with the clarification process (**Table 23**). When we look at the simple variations in the three groups it would appear that the OOM influence on the final purity is more variable than the other two and that the reducing sugars influence is the least variable within the region - that is least affected by changes in processing.

Table 23 : Solubility coefficient of the expected true purity (Kelly and Keng 1975)

	a _{RS}	a _{Ash}	a _{OOM}
Taiwan factory	43.12	66.74	19.79
Java factory	27.80	61.94	35.39
Java F. with defecation	27.41	64.22	32.95
Java F. with sulphitation	27.21	60.31	38.21
Java F. with carbonatation	28.29	64.61	33.80

2.2.3.2 USA : *Saska, et al. (1999)*

In the first part of this study, Saska (1999) also mentioned the different target purity formulas from Australia and South Africa, and reported a formula proposed by the ASI (Audubon Sugar Institute) in 1993 :

$$P = 42.4 - 12.3 \cdot \log_{10}[(G+F)/\text{Ash}]$$

Their objective was to study the influence on the molasses exhaustion of the cooling profile and residence time (24, 36 and 48 hours) and the solids levels. The final molasses used for this study came from South America. The level of ash was particularly high (**Table 24**) and the RS/Ash ratio was thus quite low (0.4).

Concentration was conducted in a 150 L vacuum pan. The three pilot crystallizers are 100 L capacity, jacketed (steam and tap water cooler) and equipped with a variable speed internal horizontal stirrer and a Honeywell temperature controller and recorder.

Table.24: : Components of cane molasses from Louisiana (Saska, 1999)

	(%solids)
Solids (refractometer)	
Sucrose by HPLC	45
Glucose by HPLC	3
Fructose by HPLC	7
G+F	10
Conductivity ash	25
Organics non sugars	20
total polysaccharides	2.00
dextran	0.50
starch	0.41
RS/Ash	0.4

Method :

- Starting with final molasses of low purity (45), pure liquid sugar was added to obtain the desired purity for the experiment (51 purity): 30 kg of molasses + 5.4 kg of refined sugar solution of 60%RDS (to increase the purity) and 3 kg of water.
- Concentration under vacuum at 60-65°C to 87-92% RDS (Refractometric Dry Solids)
- Transfer into the crystallizers. To each 26-28 kg of concentrated molasses of higher purity add 18 kg of fine refined sugar.
- Masseccuite blended at 65°C for some 30 min prior to the start of cooling.
- Samples of masseccuite were taken periodically (nearly each 12 hours) and the mother liquor immediately separated with a Nutsch filter at 90 psi (6.2 bar).

- Solids were measured by refractometry, sucrose and invert by HPLC and Ash by conductimetry and viscosity of the Nutsch samples with a Brookfield HBTDV-II cone and plate (52-spindle) connected to a precision constant temperature water bath.
- 4 cooling/reheating regimes were tested :
 - A. natural temperature decreasing to 32°C in 24 hours then hold constant for 24 hours
 - B. linear cooling at 3°C/hour followed by holding at 32°C for 48 hours
 - C. linear cooling at 3°C/hour to, followed by holding at, 40°C for 48 hours followed by reheating to 55°C (at 15°C/hour) and holding at 55°C.
 - D. linear cooling at 2°C/hour to, followed by holding at, 40°C for 48 hours followed by reheating to 55°C (at 15°C/hour) and holding at 55°C.

Results :

- The final molasses purities were in the range of 46.2-38.8.
- Either with a natural cooling or a 3°C/hour linear cooling, the Nutsch purity stabilized within a few tenths of a purity point in 24 to 48 hours, faster at higher RDS (refractometric dry solids). The cooling rate did not have a significant effect on molasses exhaustion and it appeared advisable to cool the massecuite at a relatively fast rate: 3°C/hour to, followed by holding at, 40°C or lower if the consistency permits pumping the massecuite to the heater at that temperature without dilution, followed by reheating to 55°C (at 15°C/hour) and holding at 55°C up to 3 hours.
- Although each additional 24 hours of residence time may lower the purity by some 0.5 point this may not be enough to justify installing a capacity larger than that corresponding to 24 hours residence time.
- The very good correlation between 24-48 hours target purity and its RDS levels clearly demonstrates the major effect of the Nutsch (and massecuite) concentration (dry solids) on molasses exhaustion. By 1% additional RDS increase, the target purity was lowered by some 2 purity points.
- As the degree of non-Newtonian behavior was only moderate, the viscosity was measured at only one shear rate value, 2 s^{-1} . and 50°C. A correlation related RDS and consistency was proposed :

$$\text{Viscosity (at } 50^\circ\text{C and } 2\text{s}^{-1}) = 42.6 \text{ RDS} - 3681.$$
- Viscosity measured at 50°C could be the criterion for boiling down molasses and not its dry content. A measured viscosity of 200 Pa.s appeared a suitable benchmark for molasses exhaustion. Using this parameter will partially account for the effect of dextran and other high molecular weight polysaccharides on the viscosity of low grade massecuites and molasses exhaustion.

2.3 MAIN MOLASSES EXHAUSTION PARAMETERS

Very soon after we started to study the articles on molasses exhaustion we realized that this notion was indelibly linked to sucrose solubility in molasses and that it was very important to pay attention to the analytical methods and experimental protocols used. Furthermore, we realized that it was not possible to mix the results from beet and cane molasses. It is why we chose to separate the presentation of the results on beet and cane molasses and even for cane molasses to separate the results from the different countries.

Nevertheless it is now possible to outline some common points concerning the exhaustion molasses tests and results.

2.3.1 Exhaustion parameters

For both beet and cane massecuites, the viscosity/consistency is the first limiting parameter of sucrose crystallization. The massecuite viscosity is related to the mother liquor viscosity but also to the content and size of crystals as well as to the entrapped air or gas.

The molasses viscosity corresponding to the massecuite at its viscosity limit is not the same for beet and cane molasses: 10 to 30 Pa.s for beet and up to 300 Pa.s for cane. This difference may be explained as following:

- For beet molasses, viscosity is due mainly to the high solids concentration required to overtake the saturation, as sucrose solubility increases continuously with the purity decrease and the non-sucrose to water ratio.
- In cane syrups, sucrose solubility decreases regularly as purity decreases and saturation corresponds to a much lower dry solids than in beet impure syrups. Thus, it is possible to crystallize sucrose from lower purity syrups. According to the high concentration of impurity of the mother liquor, in particular in high molecular weight components (polysaccharides and dextran), the molasses separated from the massecuite at its viscosity limit has higher viscosities than beet molasses.

It is why, more often, molasses viscosity is reported as the limiting criterion in cane molasses exhaustibility whereas for beet molasses it is the sucrose solubility. And more obviously, when viscosities are compared at the same solids content, cane molasses has much higher viscosities than beet molasses.

In both cases, beet and cane, to diminish the sucrose loss in molasses, it is important to be at the highest massecuite viscosity possible. In other words, the non-sucrose to water (NS/W) ratio must be as high as possible. As the purities of beet and cane molasses are very different, NS/W values are also different from 2.8-3.2 in beet molasses and from 3 to 5 and even higher in cane molasses.

To check the quality of molasses exhaustion, the Polish test is used in beet factories whereas in cane molasses, many authors have proposed purity target formulas (**Table 25**).

Table.25 : summary of the different purity target formulas

RS/A	consistency	Exhausted purity	Reference
0.6 to 1.8	400 Pa.s at 40°C	$P_{GC} = 33.9 - 13.4 \cdot \log_{10}[(F+G)/\text{Ash}]$ $P_{GC} = 48.2 - 4.8 \cdot (F+G)/\text{Ash} - 2.2 \text{ NS/W}$	Rein and Smith 1981
0 to 0.6		$P = 43.1 - 17.5 \cdot [1 - \exp(-0.74 \cdot (F+G)/\text{Ash})]$	Smith 1995
0.7 to 2.2	100 Pa.s ⁿ at 50°C	$P_{LE} = 41.1 - 8.7 \cdot \log_{10}[\text{RS}/\text{Ash}]$ $P_{GC} = 46.9 - 0.5 \cdot [1 - \exp(-0.13 \cdot (F+G)/\text{Ash})]$	Miller et al. 1998
0.7 to 2.2	250 Pa.s ⁿ at 50°C	$P_{LE} = 39.4 - 10.6 \cdot \log_{10}[\text{RS}/\text{Ash}]$ $P_{GC} = 55.1 - 18.7 \cdot [1 - \exp(-2.6 \cdot (F+G)/A)]$	Miller et al. 1998
0.7 to 2.2	NS/W 3.2 to 4.3	Purity of the exhausted molasses decreases almost linearly with increasing NS/W ratios	Miller et al. 1998
1.1 to 1.8		Higher purity value Smith 1995 molassigenic coefficient with cane molasses : $\text{Na}^+ > \text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+$	Sahadeo 1998
0.4	200 Pa.s at 50°C, 2s ⁻¹	This consistency appears a suitable benchmark for molasses exhaustion.	Saska 1999

But attention must be paid in these comparisons, as they were obtained with different kinds of molasses and different methods to carry out the exhaustion tests. Nevertheless, most of these equations confirm that the exhausted molasses purity decreases with the increase of the reducing sugars to ash (RS/A) ratio. Some authors emphasized that there is a strong relation between the RS/A and NS/W ratios. Miller, *et al.*, (1998) suggested that this increase of RS/A induces a decrease of the molasses viscosity for the same level of NS/W. They explained this factor by the fact that the reducing sugars (organic compounds) induce less viscosity than the ash (mineral compounds). But, the observation of Miller, *et al.*, (1998) on the important variability of molasses exhaustibility which is not explained either by NS/W or RS/Ash ratios must also be recalled. *"Even with the same NS/W ratio and the same standard exhaustion procedure (cooling profile and crystal content) molasses may have purity differences in the exhausted molasses up to 3.2 units"*.

In 1999, an analytical survey of final molasses from fifteen countries was performed by the SRI (Sahadeo and Lionnet 1999). Catch samples of final molasses were received over the period July 1997 to January 1998, with most countries submitting more than one sample. The samples were analyzed for Pol, brix, dry solids (by Karl Fisher method), sugars (by high performance anion exchange chromatography), sulphated ash, K^+ , Na^+ , Ca^{++} , Mg^{++} (by atomic absorption), silica and phosphate, colour (ICUMSA method), dextran (Robert's method), starch and gums.

The results showed some similarities but also wide differences among the various molasses.

According to the results on dry solids by Karl fisher and sugar by HPAEC they calculated the target purity with the equation proposed by Smith 1995, and the target purity difference (TPD). Most TDP values ranged from +3 to +7 (**Table 26**), a range which is commonly found in South Africa.

Table 26. An analytical survey of final molasses from 15 cane producing countries (Sahadeo and Lionnet 1999).

	True Purity	Target purity	TPD
Australia	43.81	37.01	6.80
Colombia	41.72	35.54	6.18
India	35.76	33.22	2.54
Kenya	37.62	27.91	9.71
Malawi	48.00	39.16	8.84
Mauritania	41.91	37.83	4.08
Mexico	43.75	32.69	11.06
Pakistan	45.84	39.18	6.66
Reunion	43.67	37.95	5.72
South Africa	40.85	33.60	7.25
Swaziland	40.66	35.78	4.88
Tanzania	39.18	33.63	5.55
United States of America	43.34	36.87	6.47
Zambia	43.97	36.81	7.16
Zimbabwe	38.85	35.26	3.59

2.3.2 Sucrose solubility measure and exhaustion test methods

If experimental works are planned it is worthwhile to note the general procedures used in the different experimental methods.

- First the molasses sample is warmed to remove the entrained air or gas. In one case it is even diluted. In some case, if final molasses is used, its purity is increased to test a real cooling crystallization.
- The molasses is then boiled under vacuum to a consistency level measured at 40°C (Rein and Smith 1981) or 50°C (Miller et al. 1998), or to a NS/W ratio (between 2.2 and 3.4 in the Polish Test 1992, 3.4 to 4.3 by Miller et al. 1998) or to a solids level (87% by Sahadeo 1998 and from 87% to 92% RDS by Saska et al. 1999).
- The concentrated molasses is seeded with sieved refined sugar in different ratios :
250 mL of Bakers' crystal in 330 mL molasses (Rein and Smith 1981)
20% of crystal (Miller et al. 1998)
60 g in 250 g concentrated molasses (Polish test 1992)
18 kg in 26-28 kg massecuites (Saska 1999)
- The massecuite is continuously stirred (speed 1.2 to 12 rpm) and maintained at a fixed temperature for a fixed time (40°C-48 hours by Rein and Smith 1981, Sahadeo 1998) (65°C-15 hours in the Polish test 1992) or cooled with a controlled programmed temperature profile (to 50°C and 24 hours curing time for Broadfoot and Miller 1984, from 65°C to 40°C or lower and residence time up to 48 hours with regular sampling for Saska et al. 1999).
- Molasses is separated from massecuite by pressure filtration and analyzed.

2.3.3 Addition of reducing sugar to improve molasses exhaustion

At the beginning of this study one objective was to determine if addition of reducing sugars into the final massecuite before cooling would be advantageous.

- Based on our literature survey, we do not think that it would be worthwhile to deliberately add reducing sugars to improve exhaustibility of molasses as these impurities need water to be in solution and this would increase the amount of sucrose solubilized by the water.
- For the same reason, we do not think that it is recommended to enhance the formation of reducing sugars during the steps before the crystallization as it means decreasing the sucrose yield because of the sucrose lost by hydrolysis and the amount of added water needed to solubilize the non-sucrose.

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